

IN THE UNITED STATES DISTRICT COURT  
FOR THE DISTRICT OF DELAWARE

CIBA SPECIALTY CHEMICALS  
CORPORATION, a Delaware Corporation,

Plaintiff

v.

3V, INC., a Delaware Corporation,

Defendant

C.A. No. \_\_\_\_\_

**COMPLAINT**

**Jurisdiction and Venue**

1. This suit arises under the patent laws of the United States, 35 United States Code, and seeks to have this Court adjudge the validity of U.S. patent 5,658,973 pursuant to 35 U.S.C. § 291.

2. Jurisdiction of this action lies with this Court under 35 U.S.C. § 291; 35 U.S.C. § 146; 28 U.S.C. § 1331 and 28 U.S.C. § 1338(a).

3. Venue is proper in this district pursuant to 28 U.S.C. § 1391 (b) and (c).

**The Parties**

4. Plaintiff CIBA Specialty Chemicals Corporation ("CIBA") is a corporation of the State of Delaware having a principal place of business located at 540 White Plains Road, Tarrytown, New York.

5. Upon information and belief, Defendant, 3V, Inc. ("3V") is a Delaware corporation having a principal place of business at 899 Woodstock Street, Georgetown, South Carolina.

6. Upon information and belief, 3V is the assignee of all right, title and interest in U.S. Patent 5,658,973 (the '973 patent), which this case seeks to have invalidated in whole or in part. The '973 Patent relates to "Compositions for the Stabilization of synthetic polymers." The application for the '973 patent was filed on July 26, 1995; issued on August 19, 1997; and, names Giuseppe Raspanti of Bergamo, Italy, as inventor. A copy of the '973 patent is attached as Exhibit 1.

7. CIBA is the assignee of all right, title and interest in the invention relating to a "Synergistic Stabilizer Mixture" which is disclosed and claimed in U.S. Patent 6,380,286 (the '286 patent). The application for the '286 patent was filed on March 24, 1999 and issued on April 30, 2002. The '286 patent claims the benefit of U.S. application No. 08/858,191, filed April 21, 1977; U.S. application No. 08/588,164, filed January 18, 1996; and, European application EP 95810042 filed January 23, 1995. The '286 patent names Francois Gugumus as inventor. A copy of the '286 patent is attached as Exhibit 2.

8. The '286 and '973 patents are interfering patents and claim interfering subject matter.

### COUNT I

9. Ciba repeats and realleges the allegations contained in paragraphs 1 through 8 of this Complaint as if fully set forth herein.

10. This Complaint is filed pursuant to 35 U.S.C. 291 and seeks relief against 3V wherein this court will adjudge that Francois Gugumus is the first inventor of the interfering subject matter of the '973 and '286 patents and that the '973 patent is, therefore, invalid in whole or in part.

WHEREFORE, Plaintiff respectfully prays that the Court grant:

A. Judgment awarding priority to Francois Gugumus with respect to the interfering subject matter of the '973 and '286 patents.

B. Judgment ordering that the claims of the '286 patent corresponding to the interfering subject matter are to be retained in the '286 patent owned by CIBA.

C. Judgment ordering that the claims of the '973 patent corresponding to the interfering subject matter are invalid.

D. That the Clerk of this Court shall issue a certified copy of this Court's judgment for transmittal to the U.S. Patent and Trademark Office, and that the Director of the U.S. Patent and Trademark Office shall be authorized fully to implement this Court's order.

E. Judgment ordering any further relief as may be equitable and/or appropriate in order to preserve the rights of CIBA in any further or related proceedings.

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Dated: October 31, 2006

**EXHIBIT 1**

US005658973A

**United States Patent** [19]**Raspanti**[11] **Patent Number:** **5,658,973**[45] **Date of Patent:** **Aug. 19, 1997**[54] **COMPOSITIONS FOR THE STABILIZATION OF SYNTHETIC POLYMERS**[75] **Inventor:** Giuseppe Raspanti, Bergamo, Italy[73] **Assignee:** 3V Inc., Weehawken, N.J.[21] **Appl. No.:** 507,197[22] **Filed:** Jul. 26, 1995[51] **Int. Cl.<sup>6</sup>** C08K 5/54; C08K 5/3492; C08K 5/3435[52] **U.S. Cl.** 524/99; 252/405; 524/100; 524/102; 524/103[58] **Field of Search** 524/100, 99, 102, 524/103; 252/405[56] **References Cited****U.S. PATENT DOCUMENTS**

4,086,204	4/1978	Cassandrini et al.	544/198
4,108,829	8/1978	Cassandrini et al.	544/198
4,233,412	11/1980	Rody et al.	525/167
4,331,586	5/1982	Hardy	524/97
4,477,615	10/1984	Raspanti et al.	524/100
4,692,486	9/1987	Gugumus	524/100
4,863,981	9/1989	Gugumus	524/100
4,927,930	5/1990	Cantatore et al.	544/198
4,933,451	6/1990	Cantatore et al.	524/100
5,021,485	6/1991	Gugumus	524/100

**FOREIGN PATENT DOCUMENTS**

343717	11/1989	European Pat. Off.
57-38589	8/1982	Japan

**OTHER PUBLICATIONS**

Tomoyuki Kurumada, et al., "Synergism of Hindered Amine Light Stabilizers and UV-Absorbers", Polymer Degradation and Stability 19 (1987) 263-272.

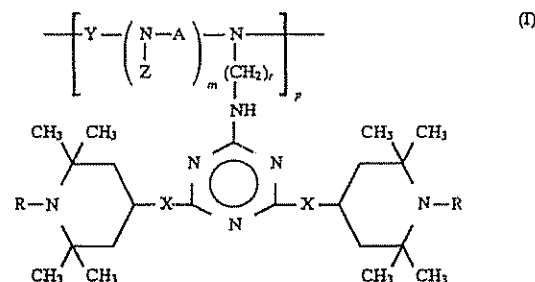
*Primary Examiner*—Veronica P. Hoke

*Attorney, Agent, or Firm*—Griffin, Butler, Whisenhunt & Kurtossy

[57] **ABSTRACT**

A composition for stabilizing synthetic polymers consisting of a blend of

a) at least a derivative of a high molecular weight polymethylpiperidine of formula (I)



wherein the groups are as defined hereinafter, and  
b) at least one other HALS stabilizer wherein the groups are as defined hereinafter is disclosed. These compositions show photostabilizing and antioxidant properties.

**15 Claims, No Drawings**

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COMPOSITIONS FOR THE STABILIZATION  
OF SYNTHETIC POLYMERS

The present invention relates to compositions consisting of mixtures of two or more different derivatives of high molecular weight polymethylpiperidine and to their use as stabilizing agents for synthetic polymers.

## BACKGROUND OF THE INVENTION

The use of compounds containing the polymethylpiperidine group, and mainly 2,2,6,6-tetramethyl-4-piperidine, for the photostabilization of polymers is well known and to this end a wide literature exists.

Generally this class of stabilizing agents is divided into two groups, namely those having low molecular weight (about 700) and those with high molecular weight (higher than 700).

A detailed disclosure of some stabilizing agents of this class, the so called hindered amines, of their different kinds and of their applicative characteristics is found in Gaechter-Mueller/Taschenbuch der Kunststoff-Additive, 2. Ausgabe 1983 pagg. 144-198.

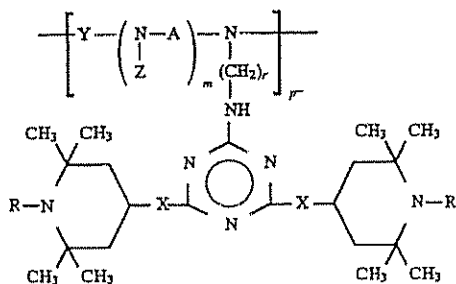
U.S. Pat. Nos. 4,692,486, 5,021,485 and EP 0080431 disclose some synergistic mixtures of derivatives of low and high molecular weight polyalkylpiperidines as photostabilizing agents for polymers. U.S. Pat. No. 4,863,981 discloses also mixtures containing two different derivatives of polymethylpiperidine, both of them having high molecular weight, as photostabilizing agents for polymers.

It has surprisingly been found that new particular combinations of compounds, all of them having high molecular weight, containing polymethylpiperidine groups, in addition to synergistic properties as photostabilizing agents, also show synergistic activity in the long term heat stabilization of synthetic polymers. As used herein, the wording "long term heat stabilization" is intended to mean that the polymer is stabilized against the degradation which occurs during the time of use of the polymer itself. As far as it is known to the applicant, said synergistic activity in the long term heat stabilization was not disclosed nor suggested in the prior art.

## DISCLOSURE OF THE INVENTION

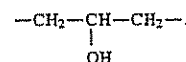
An object of the present invention is a composition for the stabilization of synthetic polymers consisting of a mixture of:

a) at least a compound of formula (I)

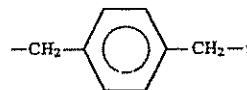


wherein R is hydrogen or methyl. X is oxygen or the N—R<sub>1</sub> group, in which R<sub>1</sub> is hydrogen or a C<sub>1</sub>–C<sub>12</sub> straight or branched alkyl. r is a number ranging from 2 to 8, included; A is —(CH<sub>2</sub>)<sub>n</sub>—, in which n can be a number from 2 to 8, the group

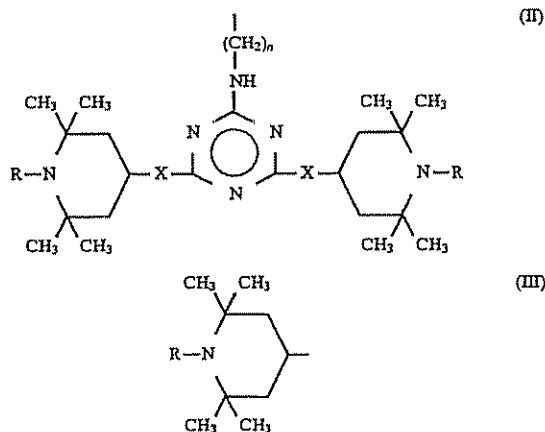
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or the group



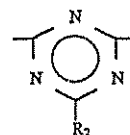
Z is hydrogen, C<sub>1</sub>–C<sub>18</sub> alkyl, the group of formula (II) or the piperidine of formula (III):



wherein R, X and n have the above defined meaning;

m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



—CO—R<sub>3</sub>—CO—; —CO—NH—R<sub>4</sub>—NH—CO— in which R<sub>2</sub> is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the

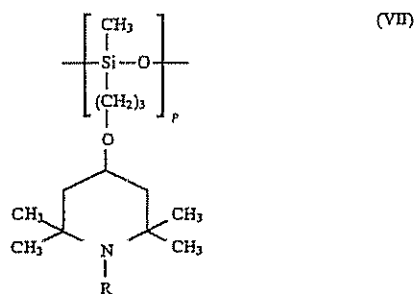
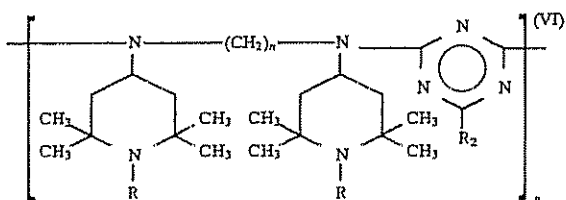
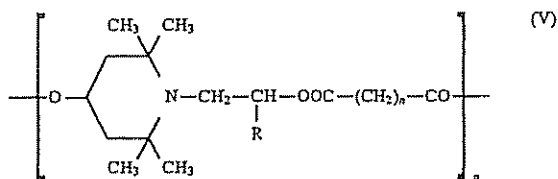
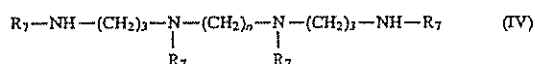
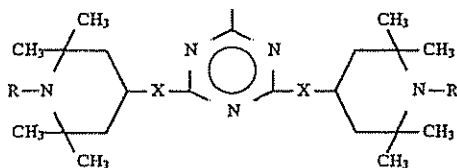


group in which R<sub>5</sub> and R<sub>6</sub> can be the same or different and are hydrogen, a C<sub>1</sub>–C<sub>18</sub> straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom which they are linked to, can form a heterocyclic ring having from 5 to 7 members, optionally containing also oxygen as heteroatom; R<sub>3</sub> is phenylene or —(CH<sub>2</sub>)<sub>n</sub>—; R<sub>4</sub> is toluylene, xylylene or —(CH<sub>2</sub>)<sub>n</sub>—, in which n has the above defined meaning; p can vary from 2 to 100; the terminal groups can be Cl or H; and

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b) at least a compound of formula (IV), (V), (VI) or (VII)

wherein  $R_7$  is a group of formula

wherein X and R are as above defined;

$R$ ,  $R_2$ ,  $n$  and  $p$  have the above meaning, the terminal groups can be hydrogen for compounds (V), chlorine or hydrogen for compounds (VI) and methyl for compounds (VII).

Examples of  $C_1$ - $C_{18}$  straight or branched alkyl group are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, pentyl, neo-pentyl, hexyl, heptyl, decyl, dodecyl, hexadecyl, octadecyl.

Examples of optionally substituted aryl group having from 6 to 14 carbon atoms are phenyl, toluyl, o-, m-, p-xylyl.

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Examples of cycloalkyl group having from 5 to 12 carbon atoms are cyclopentyl, cyclohexyl, cyclododecyl.

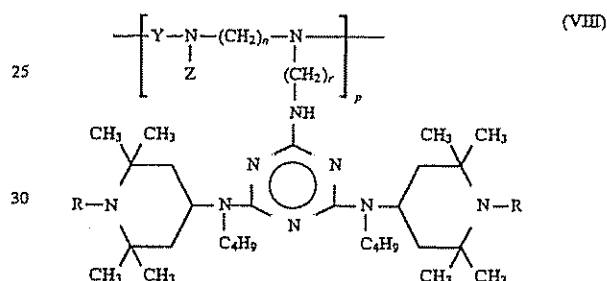
Examples of aralkyl group having from 7 to 12 carbon atoms are benzyl, 4-tert-butylbenzyl.

Examples of heterocyclic group having from 5 to 7 members are: pyrrolidine, piperidine, hexamethylenimine, morpholine.

The compounds of formula (I), (IV), (V), (VI) and (VII) are known; their methods of preparation as well as their uses as stabilizing agents are described in patents U.S. Pat. Nos. 4,477,615, 4,233,412, 4,108,829, 4,086,204, 4,331,586, EP 0255181.

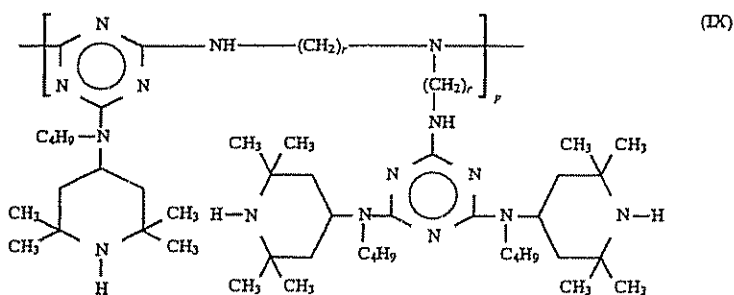
However, the stabilizing compositions according to the present invention show a photoprotective activity higher than the single components of formula (I) or (IV-VII).

In a first preferred embodiment of the present invention, the component a) is represented by the compound of formula (VIII)



wherein Z, Y, R,  $n$  and  $p$  have the above defined meaning;  $r$  is 2 or 3.

In a second preferred embodiment of the present invention, the component a) is represented by the compound of formula (IX)

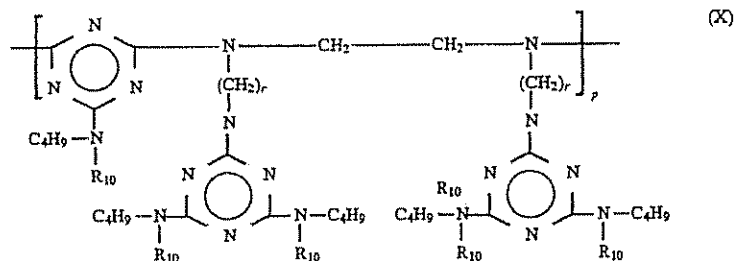


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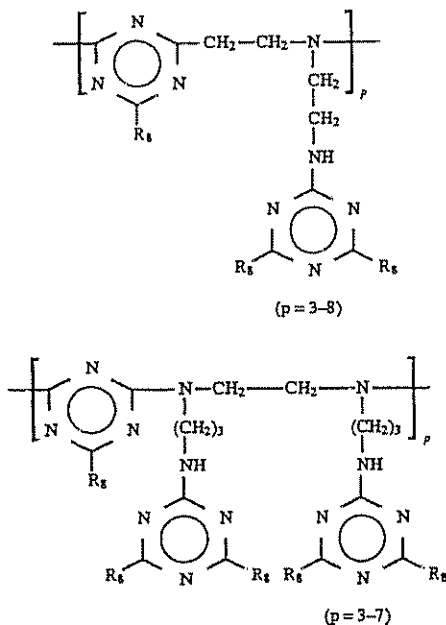
wherein  $r$  and  $p$  are as above defined.

In a third preferred embodiment of the present invention, the component a) is represented by the compound of formula (X)

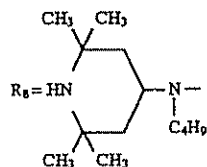


wherein  $r$  and  $p$  are as above defined,  $R_{10}$  is a group of formula (III).

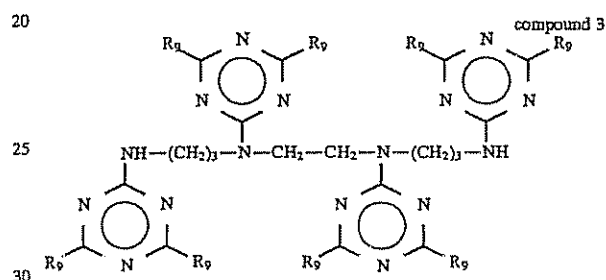
Examples of compounds of formula I are:



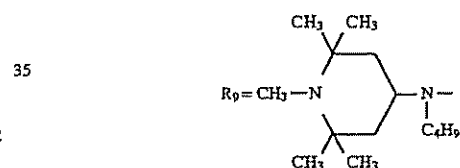
wherein



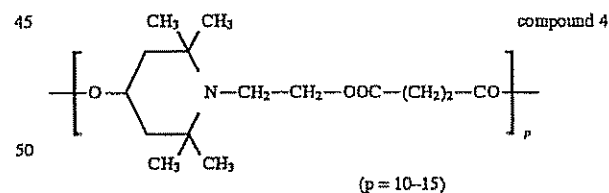
An example of compound of formula IV is:



wherein



An example of compound of formula V is:



Examples of compounds of formula VI are:

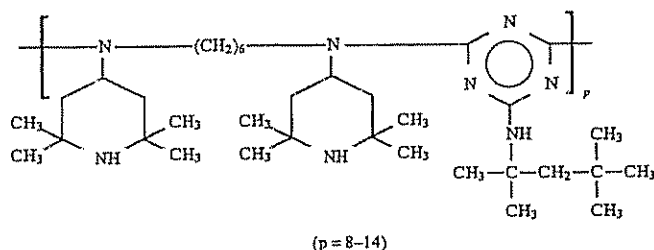
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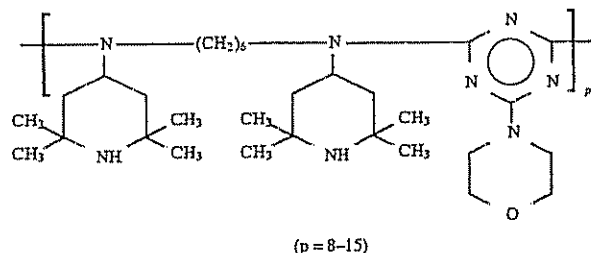
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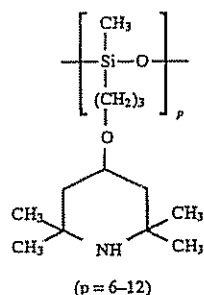


compound 5



compound 6

An example of compound of formula VII is:



compound 7

The concentration of the stabilizing compositions according to the present invention in the polymers can generally vary from 0.01 to 5% and preferably from 0.05 to 2% with respect to the weight of the polymer. Nevertheless, the stabilizing mixture can be added to the polymers also in very high amounts, for example 5-25% by weight, for the preparation of masterbatches.

The incorporation can be carried out according to various methods, for example by dry mixing the polymer with the stabilizing mixture or said mixture can be added to a suspension of the polymer to be stabilized in a suitable solvent and subsequently evaporating off the solvent.

Subsequently the polymers containing the stabilizing mixture are extruded or treated according to methods usually known in the art.

According to the present invention the compositions of compounds of formula (I) and respectively of formula (IV)-(VII) are used for the stabilization of synthetic polymers, particularly of polyolefins such as for example low and high density polyethylene, polypropylene, polymethylpentene, polyisoprene, polystyrene, polymethylstyrene and copolymers thereof and/or with other vinyl monomers as for example acrylonitrile, vinyl acetate, acryl esters.

The stabilizing compositions according to the present invention can be used also together with other additives commonly used in the technology of the synthetic polymers, such as for example: antioxidants, for example those belonging to the classes of phenols, thioethers, phosphites and phosphonites; UV-absorber, for example oxanilydes, benzotriazole and benzophenone derivatives; nickel complexes;

metal deactivators, for example oxalic acid amides, plasticizers, antistatic agents, pigments, optical bleaching agents, flame retarders.

The following examples further disclose the present invention.

#### EXAMPLE 1

1.000 g of low density polyethylene (Riblene EF 2100 V-Enichem®), 2 g of n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 1 g of calcium stearate and 1 g of a stabilizing agent, according to the present invention, or of a mixture thereof in 50:50 w/w ratio, were mixed homogeneously. The mixtures were extruded at 190° C. and transformed into pellets. From these pellets, by means of pressure forming at 200° C., films of 0.2 mm thickness were obtained.

Samples of these films were subjected to UV radiation in a Weatherometer WOM Ci-65® at a black panel temperature of 63° C. In the irradiated samples the increase of the carbonyl band at 5.85 nm in the infrared was measured and the T-0.1, i.e. the time necessary to give an increase of 0.1 of the carbonyl band, was determined. The results are reported in the following Table 1.

TABLE 1

Stabilizing agent	T 0.1 (hours)
Without stabilizing agent	300
Compound 1	2100
Compound 2	2000
Compound 3	1950
Compound 4	1750
Compound 5	2100
Compound 7	1650
Compounds 1 + 3	2750
Compounds 1 + 4	2850
Compounds 1 + 5	2650
Compounds 2 + 5	2800
Compounds 1 + 7	2600
Compounds 4 + 5 (according to US 4 863 981)	2800

#### EXAMPLE 2

Homogeneous mixtures, consisting of 1.000 g of polypropylene, (Moplen FLF 20-Himont®), 1 g of 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 0.5 g

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of calcium stearate and 2 g of a stabilizing agent or of a 50:50 mixture thereof were prepared. The mixtures were extruded at 250° C. and granulated. From these, by means of pressure forming at 260° C., 1 mm thickness-test pieces were obtained.

The so obtained test pieces were subjected to atmospheric oxygen action by heating at 130° C. in a forced air circulation oven.

The degradation was evaluated by determining the time necessary for the "chalky" appearance on test pieces.

The results are reported in the following Table 2.

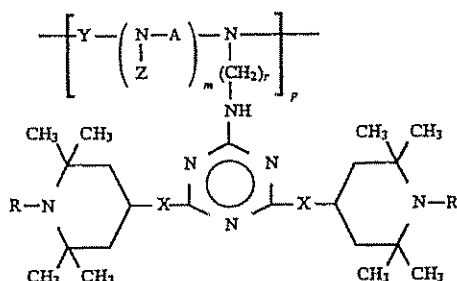
TABLE 2

Stabilizing agent	T (days)
Without stabilizing agent	34
Compound 1	55
Compound 2	57
Compound 3	49
Compound 4	54
Compound 5	57
Compound 7	41
Compounds 1 + 3	85
Compounds 2 + 4	81
Compounds 1 + 5	80
Compounds 2 + 5	78
Compounds 1 + 7	76
Compounds 4 + 5 (according to US 4 863 981)	58

I claim:

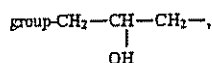
1. A composition for the stabilization of synthetic polymers comprising an about 1:1 ratio of the following components a) and b) wherein:

a) is at least one compound of formula (I)

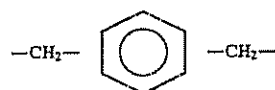


wherein R is hydrogen or methyl, X is oxygen or the group N—R<sub>1</sub>, in which R<sub>1</sub> is hydrogen or C<sub>1</sub>–C<sub>12</sub> straight or branched alkyl group, r is a number ranging from 2 to 8, included;

A is —(CH<sub>2</sub>)<sub>n</sub>—, in which n can be a number from 2 to 8, the

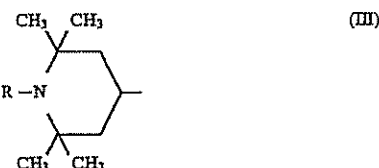
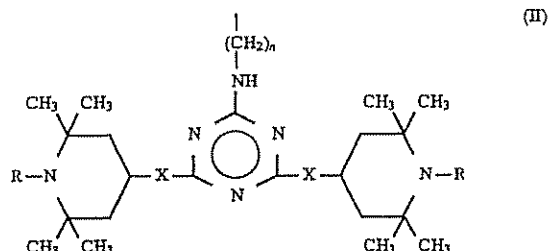


or the group



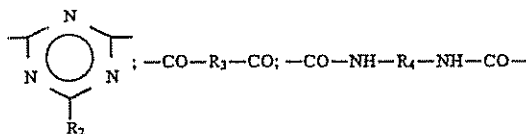
Z is hydrogen, C<sub>1</sub>–C<sub>18</sub> alkyl, the group of formula (II) or the piperidine of formula (III)

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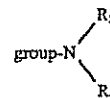


wherein R, X and n have the meaning above defined; m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



in which R<sub>2</sub> is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which R<sub>5</sub> and R<sub>6</sub> can be the same or different and are hydrogen, a C<sub>1</sub>–C<sub>18</sub> straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

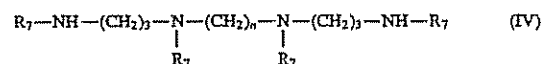
R<sub>3</sub> is phenylene or —(CH<sub>2</sub>)<sub>n</sub>—;

R<sub>4</sub> is toluylene, xylylene or —(CH<sub>2</sub>)<sub>n</sub>—, in which n has the above defined meaning.

p can range from 2 to 100;

the terminal groups can be Cl or H; and

b) is at least one compound of formula (IV), (V); (VI) or (VII)

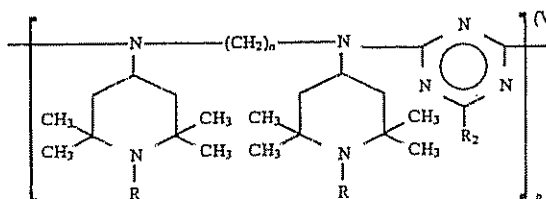


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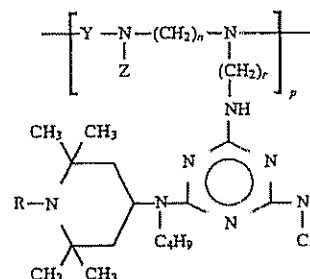


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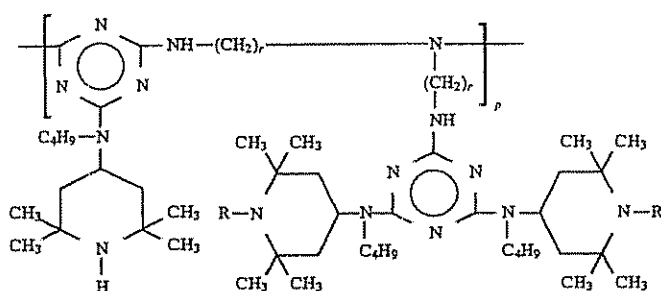
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(VII)

wherein Z, Y, R, n and p are as above defined, r is 2 or 3.

3. A composition according to claim 1, wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)

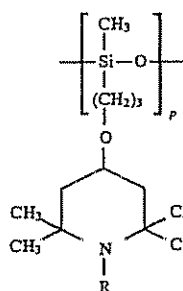


(IX)

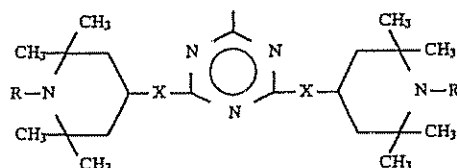
wherein r and p are as above defined.

4. A composition according to claim 1, wherein a) is a  
35 compound of formula (X) and b) is a compound of formula  
(IV)-(VII)

(VI)

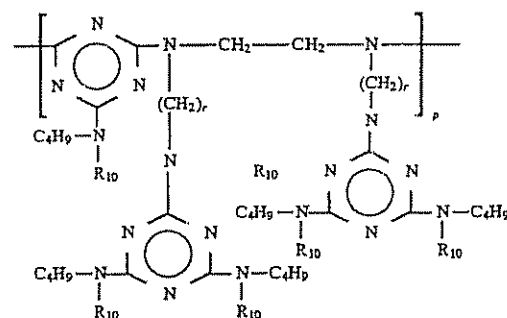


wherein  $R_7$  is a group of formula



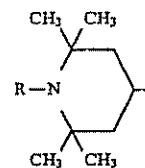
wherein R, X, n and p are as above identified.

2. A composition according to claim 1, wherein said compound a) is a compound of formula (VIII), and said compound b) is a compound of formula (IV)-(VII)



(X)

wherein  $r$  and  $p$  are as above defined and  $R_{10}$  is a group of formula (III)



(11)

wherein R is as above defined.

5. Masterbatch for the stabilization of synthetic polymers containing from 5 to 25% by weight of composition of claim 1.

6. A composition according to claim 1, consisting of a) and b).

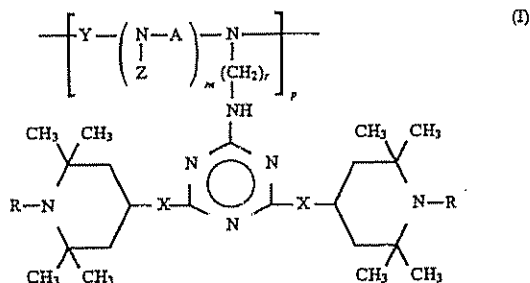
7. A method for stabilizing synthetic polymers, comprising the step of adding to a polyolefin an effective stabilizing

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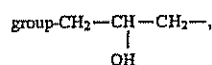
amount of a composition comprising an about 1:1 ratio of the following components a) and b) wherein:

a) is at least one compound of formula (I)

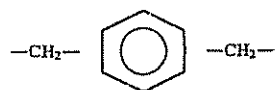


wherein R is hydrogen or methyl, X is oxygen or the group  $N-R_1$ , in which  $R_1$  is hydrogen or  $C_1-C_{12}$  straight or branched alkyl group, r is a number ranging from 2 to 8, included;

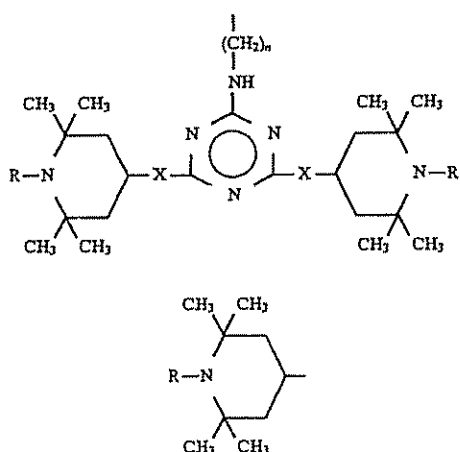
A is  $-(CH_2)_n-$ , in which n can be a number from 2 to 8, the



or the group



Z is hydrogen,  $C_1-C_{18}$  alkyl, the group of formula (II) or the piperidine of formula (III)

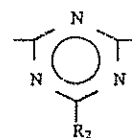


wherein R, X and n have the meaning above defined;

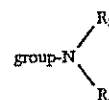
m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups

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$-\text{CO}-R_3-\text{CO}-$ ;  $-\text{CO}-\text{NH}-R_4-\text{NH}-\text{CO}-$  in which  $R_2$  is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which  $R_5$  and  $R_6$  can be the same or different and are hydrogen, a  $C_1-C_{18}$  straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

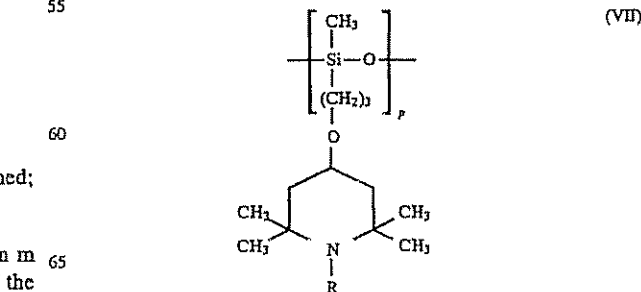
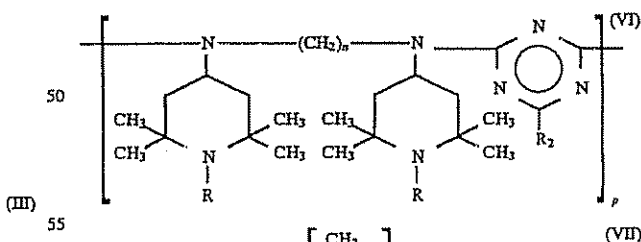
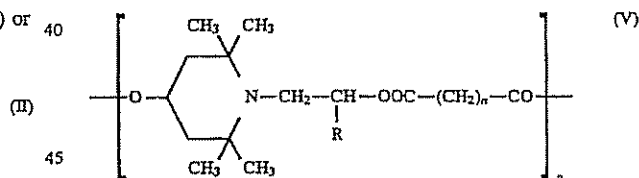
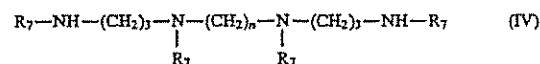
$R_3$  is phenylene or  $-(CH_2)_n-$ ;

$R_4$  is toluylene, xylylene or  $-(CH_2)_n-$ , in which n has the above defined meaning,

p can range from 2 to 100;

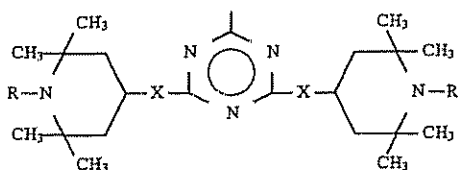
the terminal groups can be Cl or H; and

b) at least a compound of formula (IV), (V), (VI) or (VII)



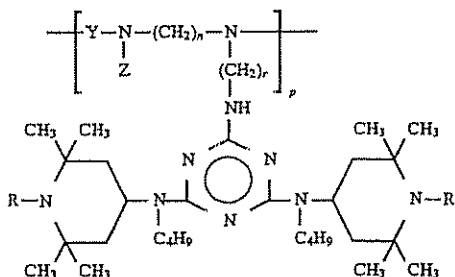
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wherein R<sub>7</sub> is a group of formula

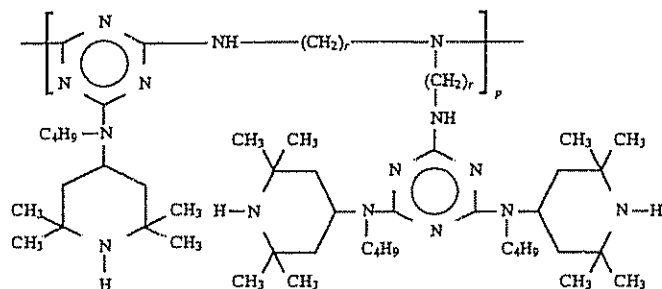
wherein R, X, n and p are as above identified.

8. A method for stabilizing synthetic polymers, according to claim 7, wherein said compound a) is a compound of formula (VIII).



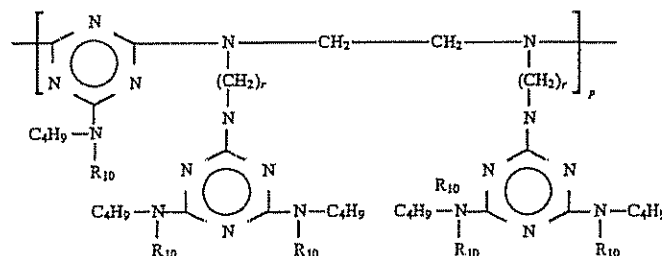
wherein X, Y, R, n and p are as above defined, r is 2 or 3.

9. A method according to claim 7, wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)



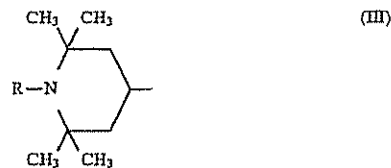
wherein r and p are as above defined.

10. A method according to claim 7, wherein a) is a compound of formula (X) and b) a compound of formula (IV)-(VII)



wherein r and p are as above defined and R<sub>10</sub> is a group of formula (III)

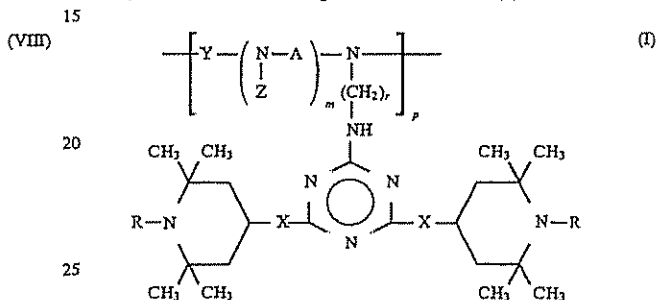
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wherein R is as above defined.

11. A stabilized polymer comprising a polyolefin and a composition for the stabilization of synthetic polymers comprising an about 1:1 ratio of the following components a) and b) wherein:

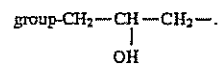
a) is at least one compound of formula (I)



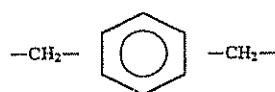
wherein R is hydrogen or methyl. X is oxygen or the group N-R<sub>1</sub>, in which R<sub>1</sub> is hydrogen or C<sub>1</sub>-C<sub>12</sub> straight or branched alkyl group, r is a number ranging from 2 to 8, included;

(IX)

A is -(CH<sub>2</sub>)<sub>n</sub>-, in which n can be a number from 2 to 8, the

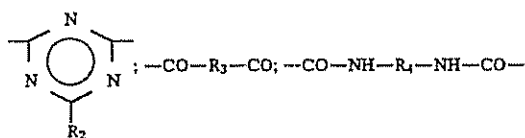


or the group



The chemical structure shows a central 1,3,5-triazine ring. Attached to the 2 and 4 positions of the triazine ring are two 4,4-dimethyl-1-piperidyl groups via methylene linkers (X). The piperidine rings are substituted with two methyl groups at the 4-position. The triazine ring is also substituted with a (CH<sub>2</sub>)<sub>n</sub> group at the 6-position and a hydrogen atom at the 1-position.

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups

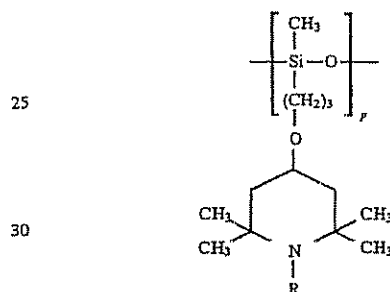
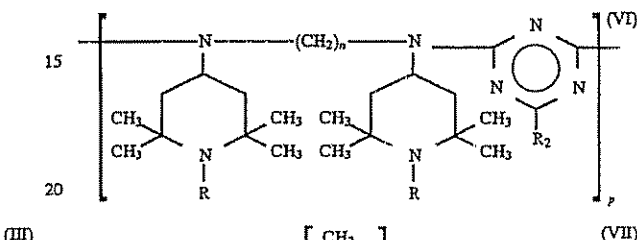
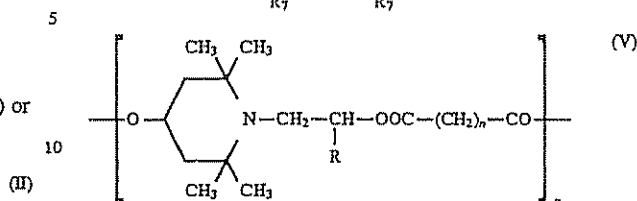
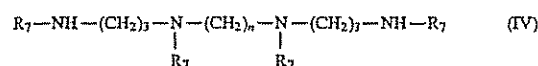

$$\begin{array}{c} \text{R}_5 \\ \diagup \\ \text{group-N} \\ \diagdown \\ \text{R}_6 \end{array}$$

$R_3$  is phenylene or  $-(CH_2)_n-$ ;

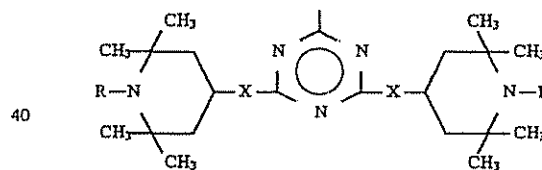
$R_4$  is toluylene, xylylene or  $-(CH_2)_n-$ , in which n has the above defined meaning,

the terminal groups can be Cl or H; and

b) at least a compound of formula (IV), (V); (VI) or (VII)

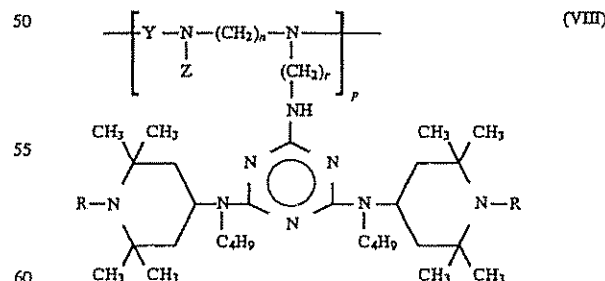


wherein R<sub>7</sub> is a group of formula



wherein R, X, n and p are as above identified.

12. A stabilized polymer according to claim 11 wherein said compound a) is a compound of formula (VIII), and said compound b) is a compound of formula (IV)-(VII)



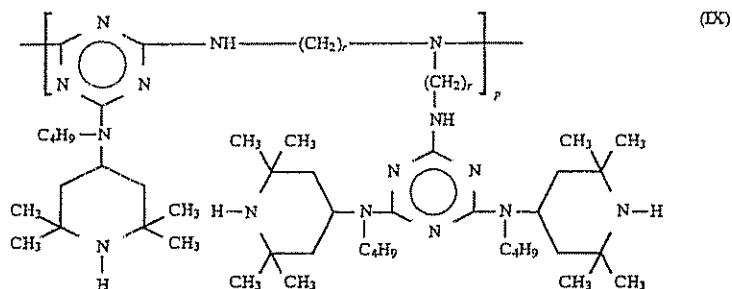
wherein Z, Y, R, n and p are as above defined, r is 2 or 3.

65 13. A stabilized polymer according to claim 11 wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)

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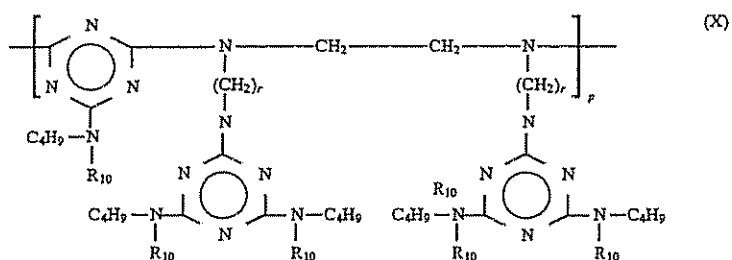


wherein  $r$  and  $p$  are as above defined.

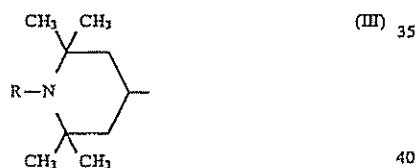
14. A stabilized polymer according to claim 11 wherein a) is a compound of formula (X) and b) is a compound of formula (IV)-(VII)

15 wherein  $R$  is as above defined.

15. A stabilized polymer according to claim 11 wherein said composition is present in an amount from 0.01 to 5% w-w.



wherein  $r$  and  $p$  are as above defined and  $R_{10}$  is a group of formula (III)



\* \* \* \* \*

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## **EXHIBIT 2**





US006380286B1

(12) **United States Patent**  
**Gugumus**

(10) Patent No.: **US 6,380,286 B1**  
(45) Date of Patent: **Apr. 30, 2002**

(54) **SYNERGISTIC STABILIZER MIXTURE**

(75) Inventor: **François Gugumus, Allschwil (CH)**

(73) Assignee: **Ciba Specialty Chemicals Corporation, Tarrytown, NY (US)**

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/275,859**

(22) Filed: **Mar. 24, 1999**

**Related U.S. Application Data**

(62) Division of application No. 08/858,191, filed on Apr. 21, 1997, now Pat. No. 6,015,849, which is a continuation of application No. 08/588,164, filed on Jan. 18, 1996, now abandoned.

(30) **Foreign Application Priority Data**

Jan. 23, 1995 (EP) 95810042

(51) Int. Cl.<sup>7</sup> C08K 5/54

(52) U.S. Cl. 524/100; 524/99; 524/102; 524/103

(58) Field of Search 524/99, 100, 102, 524/103

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Chem Abstr 111:58964u.

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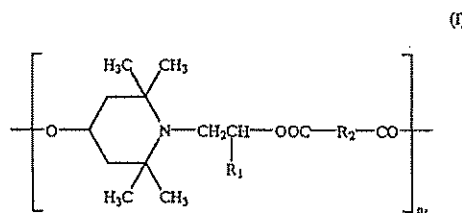
Research Disclosure, Jan. 1993, No. 345.

Primary Examiner—Veronica P. Hoke

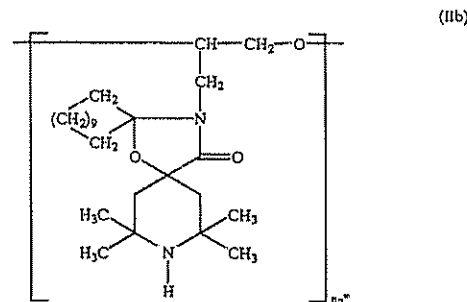
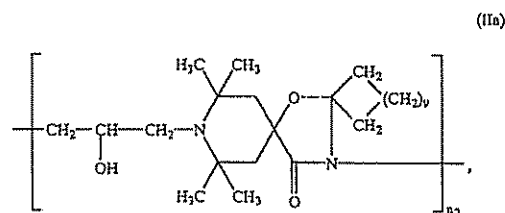
(74) Attorney, Agent, or Firm—Tyler A. Stevenson

(57) **ABSTRACT**

A synergistic stabilizer mixture comprising a component a) and, for example, a component b), where component a) is at least one compound of the formula I



in which R<sub>1</sub> is hydrogen or methyl, R<sub>2</sub> is a direct bond or C<sub>1</sub>-C<sub>10</sub>alkylene, and n<sub>1</sub> is a number from 2 to 50; component b) is at least one compound of the formulae IIa and IIb



in which n<sub>2</sub> and n<sub>2</sub>\* are a number from 2 to 50.

14 Claims, No Drawings

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## SYNERGISTIC STABILIZER MIXTURE

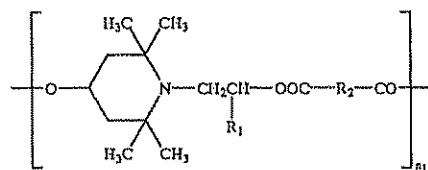
This a divisional of application Ser. No. 08/858,191, filed Apr. 21, 1997, now U.S. Pat. No. 6,015,849, which is a continuation of application Ser. No. 08/588,164, filed Jan. 18, 1996, abandoned.

The present invention relates to a stabilizer system comprising two specific high-molecular-weight polyalkylpiperidine derivatives, to the use of this stabilizer system for stabilizing organic material, and to the organic material protected against thermal, oxidative or light-induced degradation by means of the stabilizer system mentioned.

U.S. Pat. Nos. 4,692,486, 4,863,981, 4,957,953, WO-A-92/12 201, EP-A-449 685, EP-A-632 092, GB-A-2 267 499 and Research Disclosure 34549 (January 1993) describe stabilizer mixtures comprising two polyalkylpiperidine derivatives

The present invention relates to a stabilizer mixture comprising a component a) and a component b), c), d) or e), where

component a) is at least one compound of the formula I



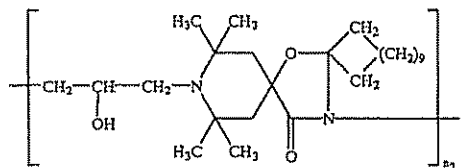
in which

$R_1$  is hydrogen or methyl,

$R_2$  is a direct bond or  $C_1-C_{10}$ alkylene and

$n_1$  is a number from 2 to 50;

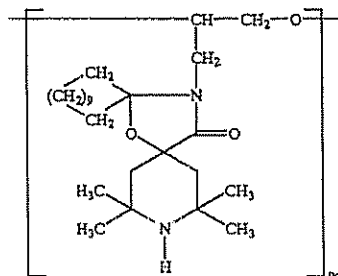
component b) is at least one compound of the formulae IIa and IIb



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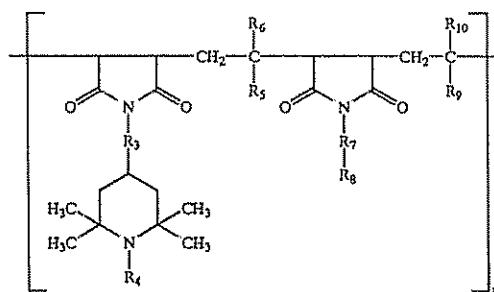
(IIb)



in which  $n_2$  and  $n_2^*$  are a number from 2 to 50;

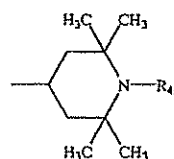
component c) is at least one compound of the formula III

(III)



in which  $R_3$  and  $R_7$ , independently of one another, are direct bond or an  $-N(X_1)-CO-X_2-CO-N(X_2)-$  group, where  $X_1$  and  $X_2$ , independently of one another, are hydrogen,  $C_1-C_8$ alkyl,  $C_5-C_{12}$ cycloalkyl, phenyl,  $C_7-C_9$ phenylalkyl or a group of the formula IV

(IV)



and  $X_2$  is a direct bond or  $C_1-C_4$ alkylene,  $R_4$  is hydrogen,  $C_1-C_8$ alkyl,  $O^-$ ,  $-CH_2CN$ ,  $C_3-C_6$ alkenyl,  $C_7-C_9$ phenylalkyl,  $C_7-C_9$ phenylalkyl which is substituted by  $C_1-C_4$ alkyl on the phenyl radical, or  $C_1-C_8$ acyl,

$R_5$ ,  $R_6$ ,  $R_9$  and  $R_{10}$ , independently of one another, are hydrogen,  $C_1-C_{30}$ alkyl,  $C_5-C_{12}$ cycloalkyl or phenyl,

$R_8$  is hydrogen,  $C_1-C_{30}$ alkyl,  $C_5-C_{12}$ cycloalkyl,  $C_7-C_9$ phenylalkyl, phenyl or a group of the formula IV, and

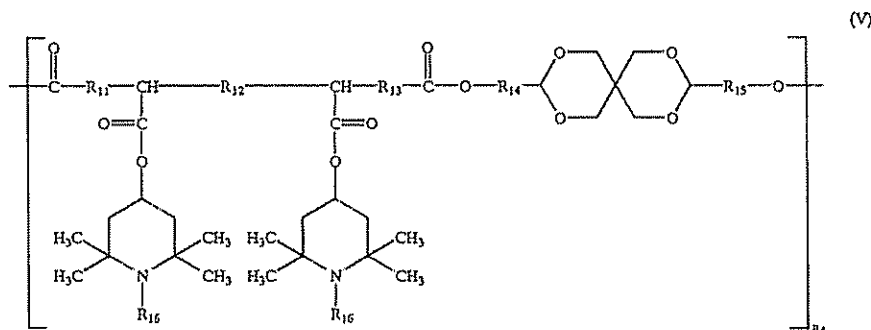
$n_3$  is a number from 1 to 50;

component d) is at least one compound of the formula V

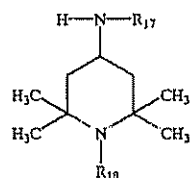
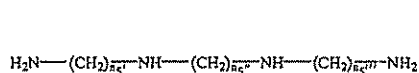
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in which  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$ ,  $R_{14}$  and  $R_{15}$ , independently of one another, are a direct bond or  $C_1$ - $C_{10}$ alkylene,  $R_{16}$  is as defined for  $R_4$ , and  $n_4$  is a number from 1 to 50; and component e) is a product obtainable by reacting a product, obtained by reacting a polyamine of the formula VIa with cyanuric chloride, with a compound of the formula VIb



in which  $n_5'$ ,  $n_5''$  and  $n_5'''$ , independently of one another, are a number from 2 to 12,  $R_{17}$  is hydrogen,  $C_1$ - $C_{12}$  alkyl,  $C_5$ - $C_{12}$  cycloalkyl, phenyl or  $C_7$ - $C_{10}$  phenylalkyl, and  $R_{18}$  is as defined for  $R_4$ .

$n_5'$ ,  $n_5''$  and  $n_5'''$  are preferably from 2 to 4,  $R_{17}$  is  $C_1$ - $C_4$ alkyl, and  $R_{18}$  is preferably hydrogen.

Examples of  $C_1$ – $C_{10}$ alkylene are methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene, hexamethylene, trimethylhexamethylene, octamethylene and decamethylene.  $R_2$  is preferably ethylene,  $R_{11}$  and  $R_{13}$  are preferably methylene,  $R_{14}$  is preferably 2,2-dimethylethylene, and  $R_{15}$  is preferably 1,1-dimethylethylene.

Examples of alkyl having up to 30 carbon atoms are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, 60  
tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl,  
1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl,  
isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl,  
3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 65  
1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl,  
1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl.

tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl, docosyl and triacontyl. One of the preferred meanings of  $R_4$ ,  $R_6$ ,  $R_{10}$ ,  $R_{16}$  and  $R_{18}$  is  $C_1$ - $C_4$ alkyl, in particular methyl. One of the preferred meanings of  $R_5$  and  $R_9$  is  $C_1$ - $C_{25}$ alkyl, in particular  $C_{15}$ - $C_{25}$ alkyl, for example hexadecyl and  $C_{18}$ - $C_{22}$ alkyl. One of the preferred meanings of  $R_8$  is  $C_1$ - $C_8$ alkyl, in particular octadecyl

Examples of  $C_5$ - $C_{12}$ cycloalkyl are cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl and cyclododecyl.  $C_5$ - $C_6$ cycloalkyl, in particular cyclohexyl, is preferred. Examples of  $C_7$ - $C_9$ phenylalkyl are benzyl and phenylethyl.

C<sub>7</sub>-C<sub>9</sub>phenylalkyl which is substituted by C<sub>1</sub>-C<sub>4</sub>alkyl on the phenyl radical is, for example, methylbenzyl, dimethylbenzyl, trimethylbenzyl or tert-butylbenzyl.

Examples of C<sub>3</sub>-C<sub>6</sub>alkenyl are allyl, 2-methallyl, butenyl, pentenyl and hexenyl. Allyl is preferred.

C<sub>1</sub>-C<sub>8</sub>acyl is preferably C<sub>1</sub>-C<sub>8</sub>alkanoyl, C<sub>3</sub>-C<sub>8</sub>alkenoyl or benzoyl. Examples are formyl, acetyl, propionyl, butyryl, pentanoyl, hexanoyl, octanoyl, benzoyl, acryloyl and crotonyl.

One of the preferred meanings of  $R_5$  and  $R_6$  is phenyl.  $X_7$  and  $R_{17}$  are preferably a direct bond.

$X_1$ ,  $X_3$ ,  $R_4$ ,  $R_{16}$  and  $R_{18}$  are preferably hydrogen.

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followed by reaction of the resultant product with a 2,2,6,6-tetramethyl-4-piperidylamine of the formula VIb. The molar ratio between 2,2,6,6-tetramethyl-4-piperidylamine and polyamine of the formula VIa is, for example, from 4:1 to 8:1. The amount of 2,2,6,6-tetramethyl-4-piperidylamine can be added in one portion or in more than one portion at intervals of a few hours.

The polyamine of the formula VIa:cyanuric chloride:2,2,6,6-tetramethyl-4-piperidylamine of the formula VIb ratio is preferably from 1:3:5 to 1:3:6.

The following example indicates one way of preparing the preferred component e).

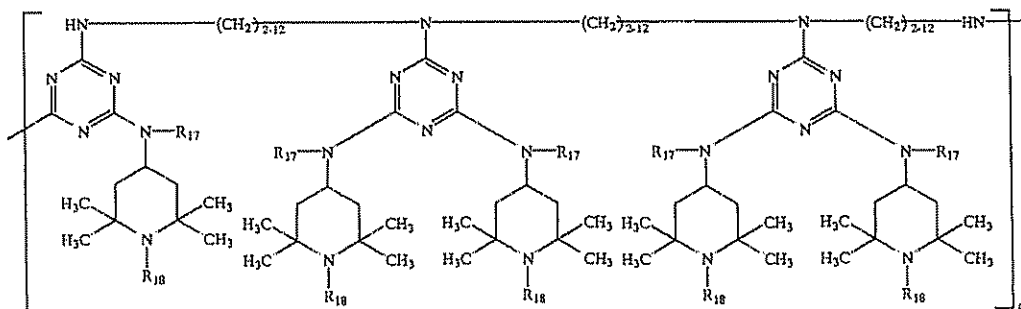
Example: 23.6 g (0.128 mol) of cyanuric chloride, 7.43 g (0.0426 mol) of N,N'-bis[3-aminopropyl]ethylenediamine and 18 g (0.13 mol) of anhydrous potassium carbonate are reacted at 50° C for 3 hours with stirring in 250 ml of 1,2-dichloroethane. The mixture is warmed at room temperature for a further 4 hours. 27.2 g (0.128 mol) of

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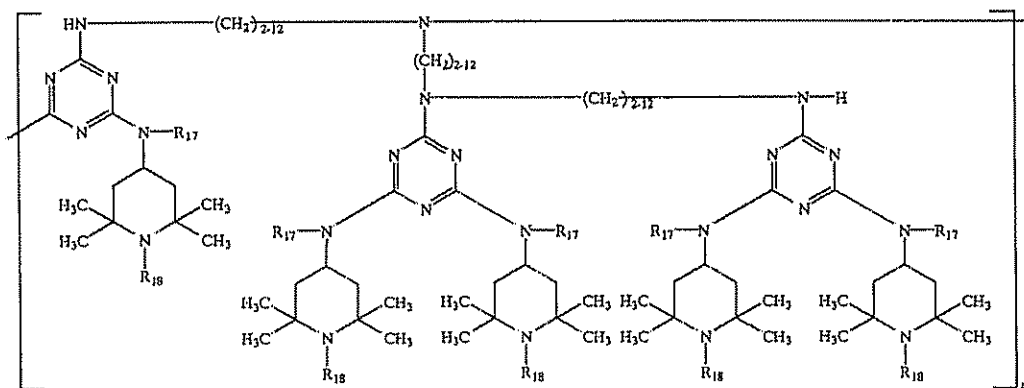
N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine are added, and the resultant mixture is warmed at 60° C for 2 hours. A further 18 g (0.13 mol) of anhydrous potassium carbonate are added, and the mixture is warmed at 60° C for a further 6 hours. The solvent is removed by distillation under a slight vacuum (200 mbar) and replaced by xylene. 18.2 g (0.085 mol) of N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine and 5.2 g (0.13 mol) of ground sodium hydroxide are added, the mixture is refluxed for 2 hours and the water formed during the reaction is removed by azeotropic distillation over a further 12 hours. The mixture is filtered. The solution is washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent is evaporated, and the residue is dried at 120–130° C in vacuo (0.1 mbar). Component e) is obtained as a colourless resin.

In general, component e) can be represented for example by a compound of the formula VI-1, VI-2 or VI-3. It can also be in the form of a mixture of these three compounds.

(VI-1)



(VI-2)



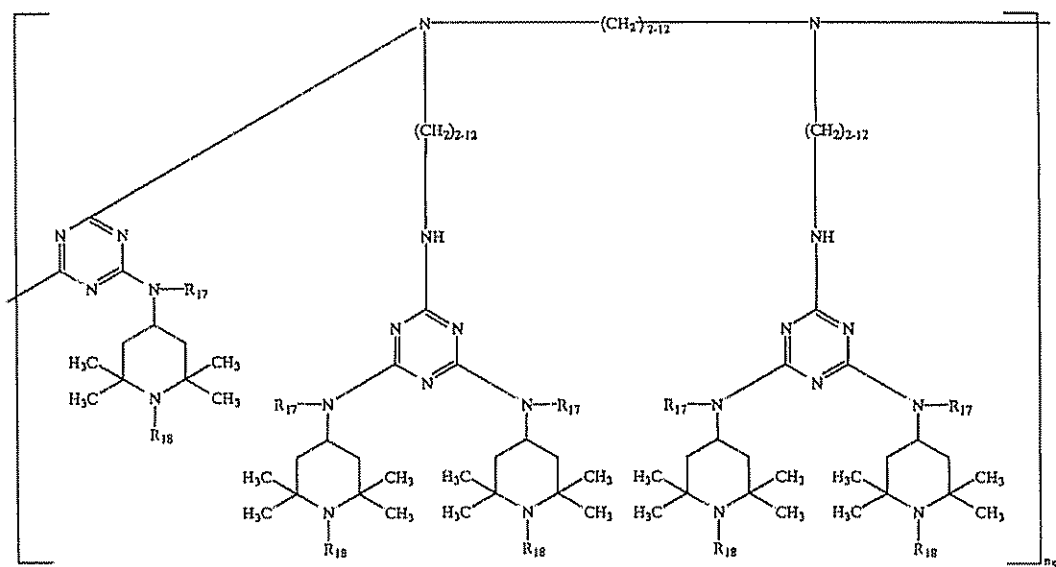
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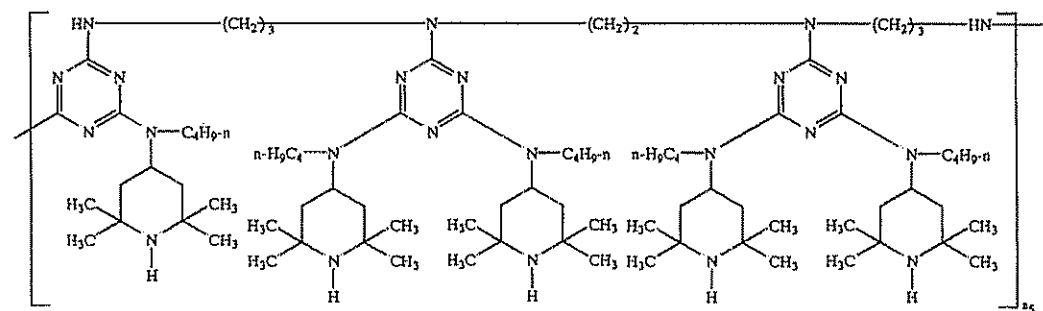
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-continued

(VI-3)



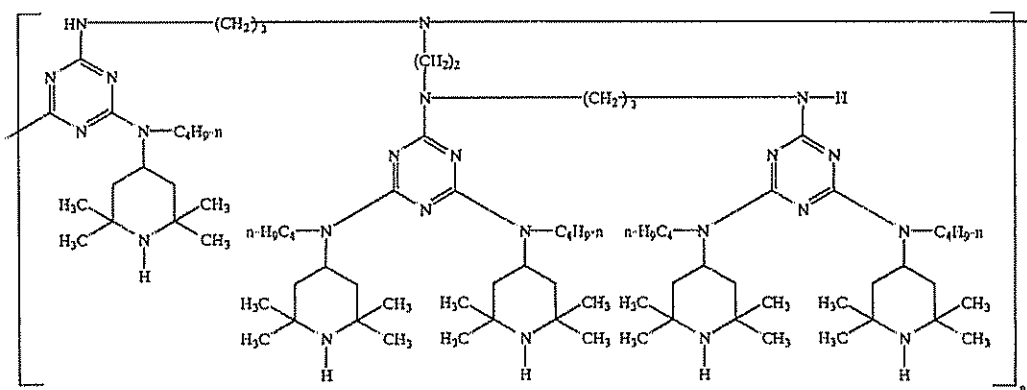
A preferred meaning of the formula VI-1 is



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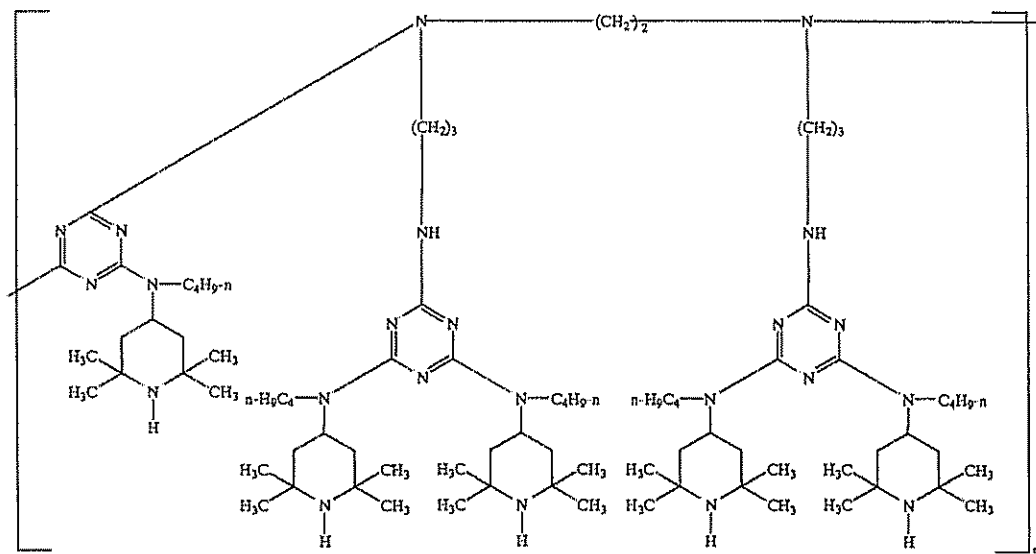
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A preferred meaning of the formula VI-2 is



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A preferred meaning of the formula VI-3 is



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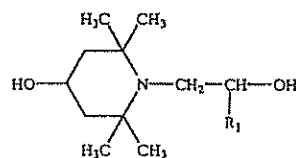
In the above formulae VI-1 to VI-3,  $n$  is preferably 1 to 20.

Component a) is preferably @TINUVIN 622, component b) is preferably @HOSTAVIN N 30, component c) is preferably @UVINUL 5050 H, @LICHTSCHUTZSTOFF UV 31 or @LUCHEM B 18, component d) is preferably @MARK LA 63 or @MARK LA 68 and component e) is preferably @UVASORB HA 88

The compounds of the formulae IIa and IIb can be obtained together as a mixture and also employed as such as component b) in the novel stabilizer system. The IIa:IIb ratio is, for example, from 20:1 to 1:20 or from 1:10 to 10:1.

The meanings of the terminal groups which saturate the free valences in the compounds of the formulae I, IIa, IIb, III, IV, V, VI-1, VI-2 and VI-3 depend on the processes used for their preparation. The terminal groups can also be modified after the preparation of the compounds.

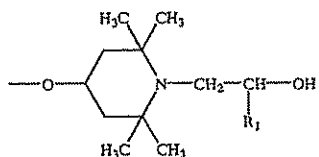
If the compounds of the formula I are prepared, for example, by reacting a compound of the formula



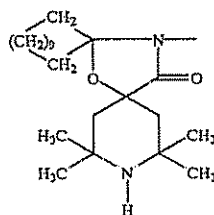
in which  $R_1$  is hydrogen or methyl, with a dicarboxylic acid diester of the formula  $Y-OOC-R_2-COO-Y$ , in which  $Y$  is, for example, methyl, ethyl or propyl, and  $R_2$  is as defined above, the terminal group bonded to the 2,2,6,6-tetramethyl-4-oxypiperidin-1-yl radical is hydrogen or  $-CO-R_2-COO-Y$ , and the terminal group bonded to the diacyl radical is  $-O-Y$  or

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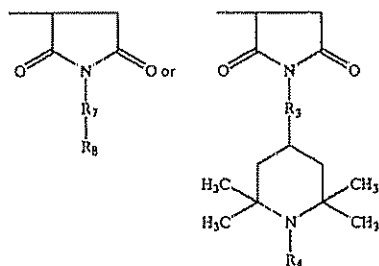
In the compounds of the formula IIa, the terminal group bonded to the nitrogen can be, for example, hydrogen and the terminal group bonded to the 2-hydroxypropylene radical can be, for example, a



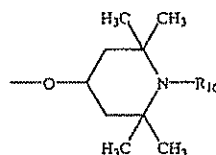
group.

In the compounds of the formula IIb, the terminal group bonded to the dimethylene radical can be, for example, —OH, and the terminal group bonded to the oxygen can be, for example, hydrogen. The terminal groups can also be polycyther radicals

In the compounds of the formula III, the terminal group bonded to the 2,5-dioxopyrrolidine ring is, for example, hydrogen, and the terminal group bonded to the —C(R<sub>p</sub>)(R<sub>10</sub>)— radical is, for example,

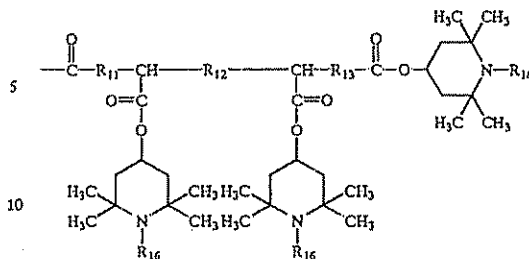


In the compounds of the formula V, the terminal group bonded to the carbonyl radical is, for example,

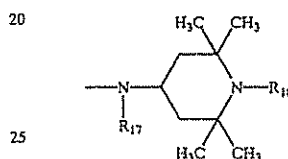


and the terminal group bonded to the oxygen radical is, for example,

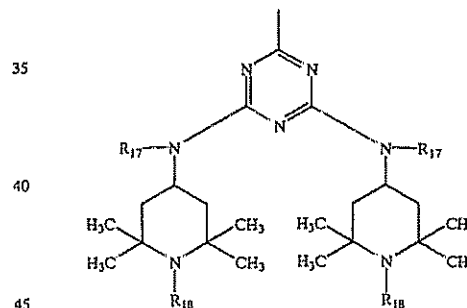
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In the compounds of the formulae VI-1, VI-2 and VI-3, the terminal group bonded to the triazine radical is, for example, Cl or a



group, and the terminal group bonded to the amino radical is, for example, hydrogen or a



group.

Preference is given to a stabilizer mixture in which R<sub>1</sub> is hydrogen, R<sub>2</sub> is ethylene, and n<sub>1</sub> is a number from 2 to 25.

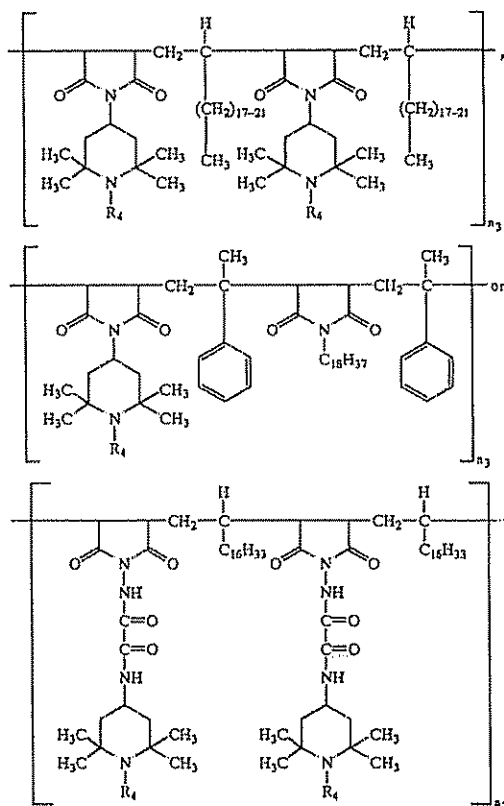
Preference is likewise given to a stabilizer mixture in which R<sub>3</sub> and R<sub>7</sub> are a direct bond or an —N(X<sub>1</sub>)—CO—X<sub>2</sub>—CO—N(X<sub>2</sub>)— group, where X<sub>1</sub> and X<sub>2</sub>, independently of one another, are hydrogen or C<sub>1</sub>–C<sub>4</sub>alkyl and X<sub>2</sub> is a direct bond, R<sub>4</sub> is hydrogen, C<sub>1</sub>–C<sub>4</sub>alkyl, OH, C<sub>6</sub>–C<sub>2</sub>alkoxy, C<sub>5</sub>–C<sub>6</sub>cycloalkoxy, allyl, benzyl or acetyl, R<sub>5</sub> and R<sub>9</sub> are C<sub>1</sub>–C<sub>25</sub>alkyl or phenyl, R<sub>6</sub> and R<sub>10</sub> are hydrogen or C<sub>1</sub>–C<sub>4</sub>alkyl, R<sub>8</sub> is C<sub>1</sub>–C<sub>25</sub>alkyl or a group of the formula IV, R<sub>11</sub>, R<sub>13</sub>, R<sub>14</sub> and R<sub>15</sub> are C<sub>1</sub>–C<sub>4</sub>alkylene, R<sub>12</sub> is a direct bond, and R<sub>16</sub> is as defined for R<sub>4</sub>.

Preference is also given to a stabilizer mixture in which component c) is at least one compound of the formula



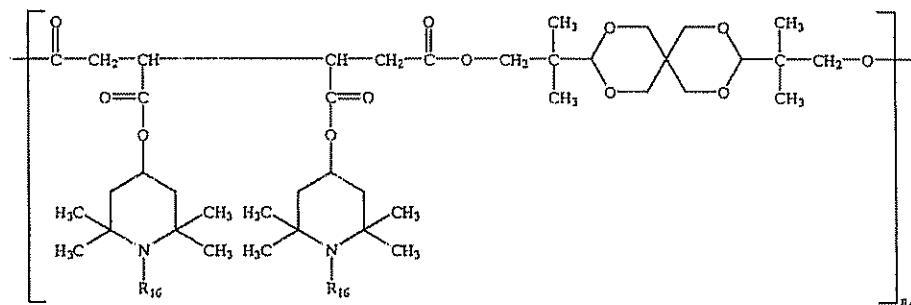
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in which  $R_4$  is hydrogen or methyl, and  $n_3$  is a number from 1 to 50.

Component d) is preferably at least one compound of the formula



in which  $R_{16}$  is hydrogen or methyl, and  $n_4$  is a number from 1 to 50.

A stabilizer mixture comprising components a) and b) is preferred. Likewise preferred is a stabilizer mixture comprising components a) and c) and a stabilizer mixture comprising components a) and d). Particular preference is given to a stabilizer mixture comprising components a) and e).

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$n_1$  is preferably from 5 to 20,  $n_2$  and  $n_3$  are preferably from 2 to 10, and  $n_4$  and  $n_5$  are preferably from 1 to 10. The following stabilizer systems are particularly preferred embodiments of the invention:

- 5 1) stabilizer mixture comprising @TINUVIN 622 and @HOSTAVIN N 30,
- 2) stabilizer mixture comprising @TINUVIN 622 and @UVINUL 5050 H,
- 3) stabilizer mixture comprising @TINUVIN 622 and @LICHTSCHUTZSTOFF UV 31,
- 10 4) stabilizer mixture comprising @TINUVIN 622 and @LUCHEM B 18,
- 5) stabilizer mixture comprising @TINUVIN 622 and @MARK LA 63,
- 15 6) stabilizer mixture comprising @TINUVIN 622 and @MARK LA 68 and
- 7) stabilizer mixture comprising @TINUVIN 622 and @UVASORB HA 88.

The novel stabilizer mixture is suitable for stabilizing organic materials against thermal, oxidative or light-induced degradation. Examples of such materials are the following:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), branched low density polyethylene (BLDPE).
2. Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

- a) radical polymerisation (normally under high pressure and at elevated temperature)
- b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb,

Vib or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either  $\pi$ - or  $\sigma$ -coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts



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- can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC)
- 2 Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).
  - 3 Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides
  - 4 Hydrocarbon resins (for example C<sub>5</sub>-C<sub>9</sub>) including hydrogenated modifications thereof (e.g. tackifiers) and mixtures of polyalkylenes and starch
  - 5 Polystyrene, poly(p-methylstyrene), poly(α-methylstyrene).
  - 6 Copolymers of styrene or α-methylstyrene with dienes or acrylic derivatives, for example styrene/butadiene, styrene/acrylonitrile, styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate, styrene/butadiene/alkyl methacrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate; mixtures of high impact strength of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and block copolymers of styrene such as styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/styrene.
  - 7 Graft copolymers of styrene or α-methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene-styrene or polybutadiene-acrylonitrile copolymers; styrene and acrylonitrile (or methacrylonitrile) on polybutadiene; styrene, acrylonitrile and methyl methacrylate on polybutadiene; styrene and maleic anhydride on polybutadiene; styrene, acrylonitrile and maleic anhydride or maleimide on polybutadiene; styrene and maleimide on polybutadiene; styrene and alkyl acrylates or methacrylates on polybutadiene; styrene and acrylonitrile on ethylene/propylene/diene terpoly-

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- mers; styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylate, styrene and acrylonitrile on acrylate/butadiene copolymers, as well as mixtures thereof with the copolymers listed under 6), for example the copolymer mixtures known as ABS, MBS, ASA or ABS polymers.
- 8 Halogen-containing polymers such as polychloroprene, chlorinated rubbers, chlorinated and brominated copolymer of isobutylene-isoprene (halobutyl rubber), chlorinated or sulfochlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.
  - 9 Polymers derived from α,β-unsaturated acids and derivatives thereof such as polyacrylates and polymethacrylates; polymethyl methacrylates, polyacrylamides and polyacrylonitriles, impact-modified with butyl acrylate
  - 10 Copolymers of the monomers mentioned under 9) with each other or with other unsaturated monomers, for example acrylonitrile/butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/alkyl methacrylate/butadiene terpolymers.
  - 11 Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine; as well as their copolymers with olefins mentioned in 1) above.
  - 12 Homopolymers and copolymers of cyclic ethers such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
  - 13 Polyacetals such as polyoxymethylene and those polyoxymethylenes which contain ethylene oxide as a comonomer; polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.
  - 14 Polyphenylene oxides and sulfides, and mixtures of polyphenylene oxides with styrene polymers or polyamides.
  - 15 Polyurethanes derived from hydroxyl-terminated polyethers, polyesters or polybutadienes on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.
  - 16 Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides starting from m-xylene diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4'-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, e.g. with polyethylene glycol, polypropylene glycol or polytetramethylene glycol; as well as polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing (RIM polyamide systems)

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- 17 Polyureas, polyimides, polyamide-imides, polyetherimides, polyesterimids, polyhydantoins and polybenzimidazoles
- 18 Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate and polyhydroxybenzoates, as well as block copolyether esters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.
- 19 Polycarbonates and polyester carbonates.
- 20 Polysulfones, polyether sulfones and polyether ketones
- 21 Crosslinked polymers derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand, such as phenolformaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins
- 22 Drying and non-drying alkyd resins.
- 23 Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability
- 24 Crosslinkable acrylic resins derived from substituted acrylates, for example epoxy acrylates, urethane acrylates or polyester acrylates.
- 25 Alkyd resins, polyester resins and acrylate resins crosslinked with melamine resins, urea resins, isocyanates, isocyanurates, polyisocyanates or epoxy resins.
- 26 Crosslinked epoxy resins derived from aliphatic, cycloaliphatic, heterocyclic or aromatic glycidyl compounds, e.g. products of diglycidyl ethers of bisphenol A and bisphenol F, which are crosslinked with customary hardeners such as anhydrides or amines, with or without accelerators.
- 27 Natural polymers such as cellulose, rubber, gelatin and chemically modified homologous derivatives thereof, for example cellulose acetates, cellulose propionates and cellulose butyrates, or the cellulose ethers such as methyl cellulose; as well as rosins and their derivatives
- 28 Blends of the aforementioned polymers (polyblends), for example PP/EPDM, Polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PBT/ABS or PBT/PET/PC.
- 29 Naturally occurring and synthetic organic materials which are pure monomeric compounds or mixtures of such compounds, for example mineral oils, animal and vegetable fats, oil and waxes, or oils, fats and waxes based on synthetic esters (e.g. phthalates, adipates, phosphates or trimellitates) and also mixtures of synthetic esters with mineral oils in any weight ratios, typically those used as spinning compositions, as well as aqueous emulsions of such materials
- 30 Aqueous emulsions of natural or synthetic rubber, e.g. natural latex or latices of carboxylated styrene/butadiene copolymers

The invention therefore furthermore relates to a composition comprising an organic material which is sensitive to oxidative, thermal or light-induced degradation and a novel stabilizer mixture.

The organic material is preferably a synthetic polymer, in particular from one of the above groups. Polyolefins are

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preferred, and polyethylene, polypropylene and copolymers thereof are particularly preferred.

The components of the novel stabilizer system can be added to the material to be stabilized either individually or mixed with one another. The components can be employed, independently of one another, in amounts of from 0.01 to 4.99%, with the proviso that the total amount of component a) and component b), c), d) or e) is from 0.02 to 5%, based on the total weight of the material to be stabilized.

The total amount of component a) and component b), c), d) or e) is preferably from 0.05 to 3%, in particular from 0.05 to 2%, or from 0.05 to 1%, based on the total weight of the material to be stabilized.

The weight ratio between component a) and component b), c), d) or e) is preferably from 20:1 to 1:20, in particular from 10:1 to 1:10, for example from 5:1 to 1:5.

The novel stabilizer mixture or the individual components thereof can be incorporated into the organic material by known methods, for example before or during shaping or by applying the dissolved or dispersed compounds to the organic material, if necessary with subsequent evaporation of the solvent. The individual components of the novel stabilizer mixture can be added to the materials to be stabilized in the form of a powder, granules or a masterbatch, which contains these components in, for example, a concentration of from 2.5 to 25% by weight.

If desired, the components of the novel stabilizer system can be melt blended with one another before incorporation in the organic material.

The novel stabilizer system or its components can be added before or during the polymerization or before the crosslinking.

The materials stabilized in this way can be used in a wide variety of forms, for example as films, fibres, tapes, moulding compositions, profiles or as binders for paints, adhesives or putties.

The stabilized organic materials of the invention may additionally also contain various conventional additives, for example:

#### 1. Antioxidants

- 1.1 Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-( $\alpha$ -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

- 1.2 Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

- 1.3 Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-di-phenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl)adipate.

- 1.4 Tocopherols, for example  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol,  $\delta$ -tocopherol and mixtures thereof (Vitamin E).

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- 1 5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-amyphenol), 4,4'-bis-(2,6-dimethyl-4-hydroxyphenyl)disulfide.
- 1 6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-( $\alpha$ -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylenedibis(4,6-di-tert-butylphenol), 2,2'-ethylenedibis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-( $\alpha$ , $\alpha$ -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.
- 1 7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.
- 1 8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis-[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.
- 1 9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.
- 1 10. Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.
- 1 11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-

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- tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.
- 1 12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.
- 1 13. Esters of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl) oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2] octane.
- 1 14. Esters of  $\beta$ -(5-tert-butyl-4-hydroxy-3-methylphenyl) propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl) oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2] octane.
- 1 15. Esters of  $\beta$ -(3,5-dicyclohexyl-4-hydroxyphenyl) propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl) oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2] octane.
- 1 16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2] octane.
- 1 17. Amides of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.
- 1 18. Ascorbic acid (vitamin C)
- 1 19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-



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N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)-diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylamino-phenol, 4-nonanoylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[2-(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, Bis[4-(1,3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-one, N,N-bis(2,2,6,6-tetramethyl-piperid-4-yl)-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2'-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-( $\alpha,\alpha$ -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-(2-ethylhexyloxy)-carbonyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-ethylhexyloxy)-carbonyl)phenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5-methylphenyl)benzotriazole, and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxy-carbonyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300;  $[R-CH_2CH_2-COO(CH_2)_3]_n$ , where R=3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl

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2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, as for example 4-tertbutylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl  $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylate, isooctyl ( $\alpha$ -cyano- $\beta,\beta$ -diphenylacrylate, methyl  $\alpha$ -carbomethoxycinnamate, methyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxy-cinnamate, butyl  $\alpha$ -cyano- $\beta$ -methyl-p-methoxy-cinnamate, methyl  $\alpha$ -carbomethoxy-p-methoxycinnamate and N-( $\beta$ -carbomethoxy- $\beta$ -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octyl-amino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitritriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediyl)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearoyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, the condensate of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearoyloxy-2,2,6,6-

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- tetramethylpiperidine, a condensation product of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl) hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimid, N-(1,2,2,6,6-pentamethyl-piperidyl)-n-dodecylsuccinimid, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxospiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4,5]decane und epichlorohydrin.
- 2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethydoxanilide, N,N'-bis(2-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethydoxanilide and its mixture with 2-ethoxy-2'-ethyl-5, 4'-di-tert-butoxanilide and mixtures of ortho- and paramethoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides
- 2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxy-phenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4(3-butoxy-2-hydroxy-propoxy)phenyl]3-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.
3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.
4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl)phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl)phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecyloxy pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)pentaerythritol diphosphite,

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- tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methylphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethylphosphite.
5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-diethylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-di-octadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine
6. Nitrones, for example, N-benzyl-alpha-phenyl-nitron, N-ethyl-alpha-methyl-nitron, N-octyl-alpha-heptyl-nitron, N-lauryl-alpha-undecyl-nitron, N-tetradecyl-alpha-tridecyl-nitron, N-hexadecyl-alpha-pentadecyl-nitron, N-octadecyl-alpha-heptadecyl-nitron, N-hexadecyl-alpha-heptadecyl-nitron, N-octadecyl-alpha-pentadecyl-nitron, N-heptadecyl-alpha-heptadecyl-nitron, N-octadecyl-alpha-hexadecyl-nitron, nitron derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.
7. Thiosynergists, for example, dilauryl thiodipropionate or distearyl thiodipropionate.
8. Peroxide scavengers, for example esters of beta-thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutylthiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(beta-dodecylmercapto)propionate.
9. Polyamide stabilisers, for example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.
10. Basic co-stabilisers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or tin pyrocatecholate.
11. Nucleating agents, for example, inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds such as ionic copolymers ("ionomers").
12. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.
13. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing, agents, antistatic agents and blowing agents.
14. Benzofuranones and indolinones, for example those disclosed in U.S. Pat. Nos. 4,325,863, 4,338,244, 5,175,312, 5,216,052, 5,252,643, DE-A-4 316 611, DE-A-4 316 622, DE-A-4 316 876, EP-A-0 589 839 or EP-A-0 591 102 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-

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benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxymethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one

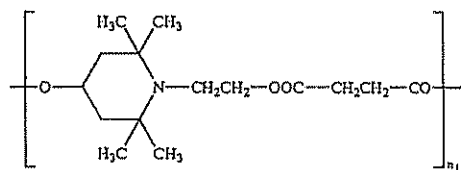
The weight ratio between the novel stabilizer mixture and the conventional additives can be, for example, from 1:0.5 to 1:5

The invention furthermore relates to the use of the novel stabilizer mixture for stabilizing organic material against oxidative, thermal or light-induced degradation.

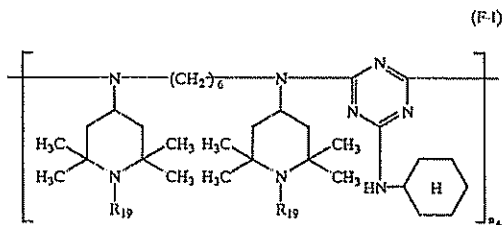
The organic materials stabilized by means of the novel stabilizer system are distinguished not only by significantly improved light stability, but also in some cases by improved thermal stability.

The foregoing also applies correspondingly to the following stabilizer mixture, which is likewise a subject-matter of the present invention:

A stabilizer mixture comprising a compound of the formula A-I



in which  $n_1$  is a number from 2 to 25, in particular from 2 to 15, and a compound of the formula F-I



in which  $R_{19}$  is hydrogen,  $C_1$ - $C_8$ alkyl, O,  $-\text{CH}_2\text{CN}$ ,  $C_3$ - $C_6$ alkenyl,  $C_7$ - $C_9$ phenylalkyl,  $C_7$ - $C_9$ phenylalkyl which is substituted by  $C_1$ - $C_4$ alkyl on the phenyl radical, or  $C_1$ - $C_8$ acyl, and  $n_2$  is a number from 2 to 25, in particular from 2 to 10.

$R_{19}$  is preferably hydrogen or  $C_1$ - $C_4$ alkyl, in particular hydrogen

The individual components of this stabilizer mixture are known and are in some cases commercially available. They can furthermore also be prepared analogously to the processes described in U.S. Pat. Nos. 4,233,412 and 4,086,204.

A stabilizer mixture comprising @TINUVIN 622 and @DASTIB 1082 is preferred.

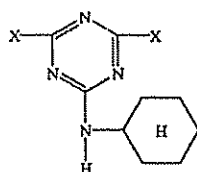
The meanings of the terminal groups which saturate the free valences in the compounds of the formulae A-I and F-I are dependent on the processes used for their preparation.

The terminal groups can also be modified after the preparation of the compounds.

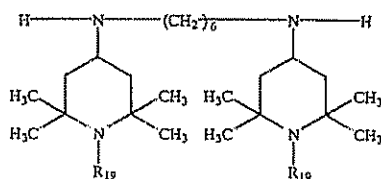
The comments made regarding the terminal groups of the compounds of the formula I apply correspondingly to the terminal groups of the compound of the formula A-I.

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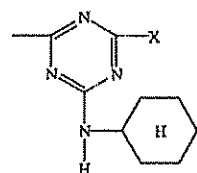
If the compound of the formula F-I is prepared by reacting a compound of the formula



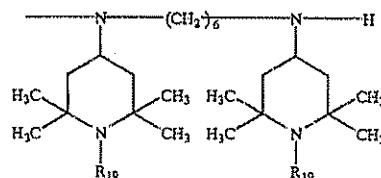
in which X is, for example, halogen, in particular chlorine, with a compound of the formula



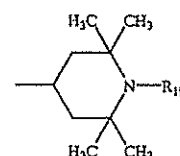
the terminal group bonded to the diamino radical is hydrogen or



and the terminal group bonded to the triazine radical is X or



If X is halogen, it is advantageous to replace this by, for example,  $-\text{OH}$  or an amino group when the reaction is complete. Examples which may be mentioned of amino groups are: pyrrolidin-1-yl, morpholino,  $-\text{NH}_2$ ,  $-\text{N}(\text{C}_1\text{-C}_8\text{alkyl})_2$  and  $-\text{NR}^*(\text{C}_1\text{-C}_8\text{alkyl})$ , in which  $\text{R}^*$  is hydrogen or a group of the formula



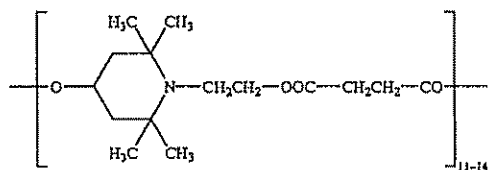
The examples below illustrate the invention in greater detail. All percentages are by weight, unless stated otherwise.

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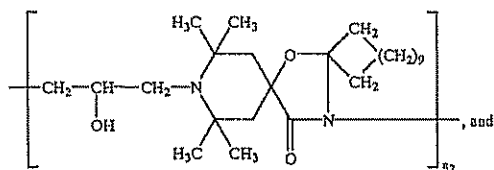
LIGHT STABILIZERS USED IN EXAMPLES 1-4

Compound A



Compound b

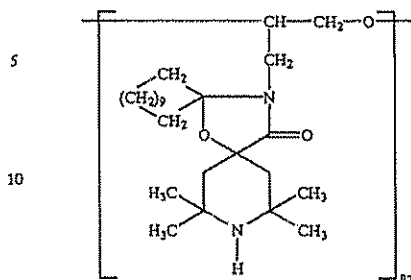
Mixture of the compounds



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-continued

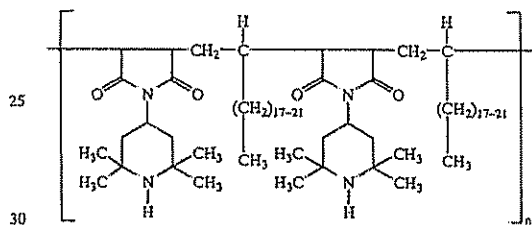
(IIb)



in which the mean value of  $n_2$  is approx. 3.9 and the mean value of  $n_2^*$  is approx. 4.2, and the ratio between (IIa) and (IIb) is approx. 4:1.

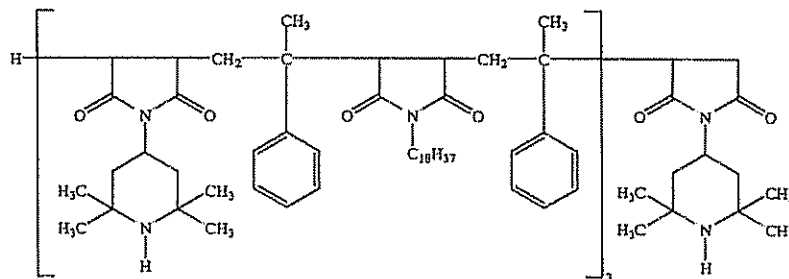
Compound C-1

(IIa)

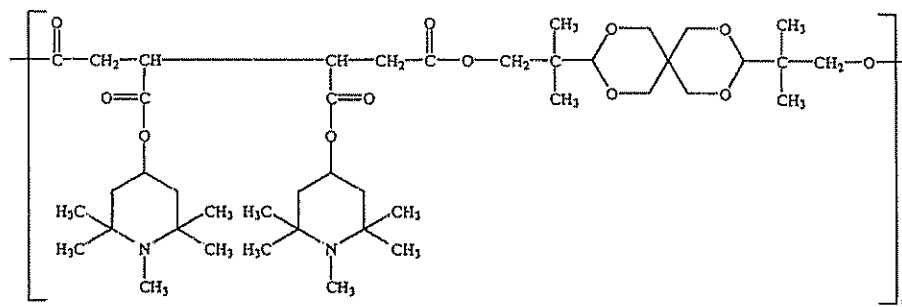


The mean value of  $n_3$  is 3.2.

Compound C-2

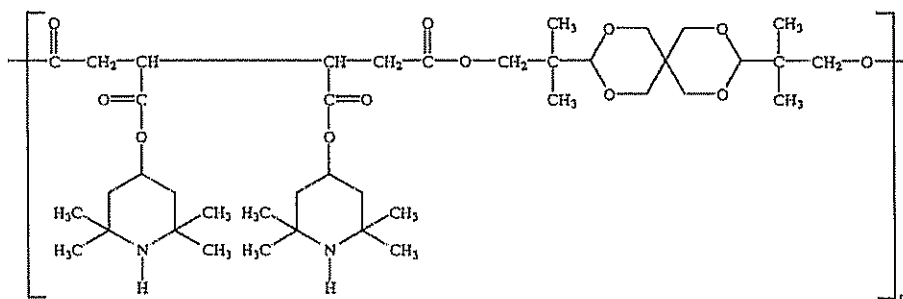


Compound D-1



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The mean value of  $n_a$  is 2.5.  
Compound D-2



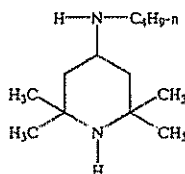
The mean value of  $n_4$  is 2.5.

### Compound E

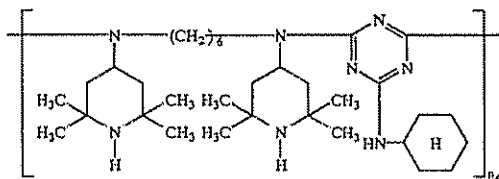
Product obtainable by reacting a product, obtained by reacting a polyamine of the formula



with cyanuric chloride, with a compound of the formula



### Compound F



The mean value of  $n_0$  is 4.4

### Example 1

### Light Stabilization Action in Polypropylene Tapes

100 parts of polypropylene powder [melt flow index 2.4 g/10 min (230° C., 2160 g)] are mixed in a tumble mixer with 0.05 part of pentaerythrityl tetrakis[ $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], 0.05 part of tris[2,4-di-*tert*-butylphenyl]phosphite, 0.1 part of calcium stearate and the amount of light stabilizer indicated in Table 1, and the mixture is subsequently granulated in an extruder at a temperature of from 180 to 220° C

The granules obtained are converted into a film in a second extruder fitted with a flat film die (temperature from 220 to 260° C.), and the film is cut into tapes, which are subsequently stretched in a ratio of 1:5.25 at elevated 65 temperature and wound up (linear density of the tapes from 700 to 900 den; tear strength from 5.5 to 6.5 g/den)

The polypropylene tapes produced in this way are mounted without tension onto sample carriers and weathered

20 in a WEATHER-O-METER Ci 65. After various times, 5  
test specimens are taken in each case and their tear strength  
is determined. The measure used for the protective action of  
the individual light stabilizers is the exposure time before  
the tear strength of the tapes drops to 50% of the initial  
25 value. The values obtained are shown in Table 1.

TABLE 1

	Hours in WEATHER-O-METER C1 65 to 50% of tear strength
30 Light stabilizer	
None	550
0.1% of compound A	2640
0.1% of compound E	3050
0.05% of compound A and 0.05% of compound E	>3100

### Example 2

### Light Stabilization Action in Polypropylene Tapes

Samples are produced analogously to the process described in Example 1. The tapes are stretched at a ratio of 1:5.25. The experimental results are shown in Table 2.

TABLE 2

	Hours in WEATHER-O-METER C 65 to 50% residual tear strength	
Light stabilizer	0.1% of light stabilizer	0.2% of light stabilizer
None	570	570
Compound A	1730	2900
Compound C-1	1900	3100
Compound C-2	1250	1500
Compound A and compound C-1 in a ratio of 1:1	2050	>3200
Compound A and compound C-2 in a ratio of 1:1	2000	>3200

### Example 3

### Light Stabilization Action in Polypropylene Block Copolymer Films

100 parts of polypropylene block copolymer powder are homogenized for 10 minutes at 200° C. in a Brabender



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plastograph with 0.05 part of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.10 part of tris (2,4-di-tert-butylphenyl)phosphite, 0.1 part of calcium stearate and the light stabilizers shown in Table 3. The composition obtained is removed from the compounder as rapidly as possible and pressed in a toggle press to give a sheet with a thickness of 2–3 mm. A piece of the resultant green pressing is cut out and pressed between two high-gloss hard aluminium foils for 6 minutes at 260° C by means of a hydraulic bench press to give a sheet with a thickness of 0.5 mm, which is immediately cooled in a water-cooled press. Pieces each measuring 60×25 mm are then stamped out of this 0.5 mm sheet and exposed to light in a WEATHER-O-METER Ci 65 (black panel temperature 63±2° C, no exposure to rain water). These test specimens are removed from the exposure apparatus at regular intervals and tested for their carbonyl content in an IR spectrometer. The increase in the carbonyl absorbance during exposure is a measure of the photooxidative degradation of the polymer and is known from experience to be associated with a deterioration in the mechanical properties. The results are shown in Table 3.

TABLE 3

Light stabilizer	Hours in WEATHER-O-METER Ci 65 to 0.2 carbonyl absorbance
0.2% of compound A	2040
0.2% of compound B	1710
0.2% of compound C-1	505
0.2% of compound E	2400
0.2% of compound F	1550
0.1% of compound A and 0.1% of compound B	2360
0.1% of compound A and 0.1% of compound C-1	1540
0.1% of compound A and 0.1% of compound E	3330
0.1% of compound A and 0.1% of compound F	2660

## Example 4

## Light Stabilization Action in High-density Polyethylene Films

100 parts of high-density polyethylene powder (density=0.965 g/cm<sup>3</sup>) are homogenized for 10 minutes at 180° C. in a Brabender plastograph with 0.033 part of pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.066 part of tris(2,4-di-tert-butylphenyl)phosphite, 0.1 part of calcium stearate and the light stabilizers shown in Table 4. The composition in the amounts obtained is removed from the compounder as rapidly as possible and pressed in a toggle press to give a sheet with a thickness of 2–3 mm. A piece of the resultant green pressing is cut out and pressed between two high-gloss hard aluminium foils for 6 minutes at 210° C. by means of a hydraulic bench press to give a sheet with a thickness of 0.5 mm, which is immediately cooled in a water-cooled press. Pieces measuring 60×25 mm are then stamped out of this 0.5 mm sheet and exposed to light in a Weather-O-meter Ci 65 (black panel temperature 63±2° C, no exposure to rain water). These test specimens are removed from the exposure apparatus at regular intervals and tested for their vinyl content in an IR spectrometer. The

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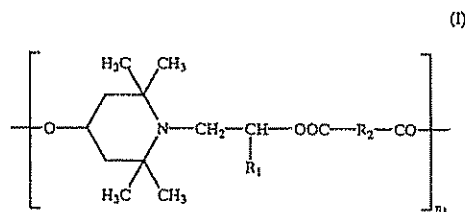
increase in the vinyl absorbance (909 cm<sup>-1</sup>) during exposure is a measure of the photooxidative degradation of the polymer and is known from experience to be associated with a deterioration in the mechanical properties. The results are shown in Table 4.

TABLE 4

Light stabilizer	Vinyl absorbance after 7222 hours in the WEATHER-OMETER Ci 65
None	0.097 after 318 hours
0.1% of compound A	0.039
0.1% of compound B	0.046
0.1% of compound C-1	0.058
0.1% of compound C-2	0.143 after 5286 hours
0.1% of compound D-1	0.040
0.1% of compound D-2	0.040
0.1% of compound E	0.054
0.1% of compound F	0.051
0.05% of compound A and 0.05% of compound B	0.036
0.05% of compound A and 0.05% of compound C-1	0.033
0.05% of compound A and 0.05% of compound C-2	0.039
0.05% of compound A and 0.05% of compound D-1	0.037
0.05% of compound A and 0.05% of compound D-2	0.034
0.05% of compound A and 0.05% of compound E	0.037
0.05% of compound A and 0.05% of compound F	0.037

What is claimed is:

1. A stabilizer mixture comprising a component a) and a component c) where component a) is at least one compound of the formula I



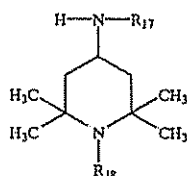
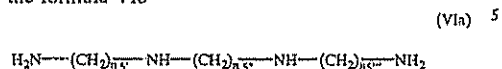
in which

R<sub>1</sub> is hydrogen or methyl,R<sub>2</sub> is a direct bond or C<sub>1</sub>–C<sub>10</sub>alkylene andn<sub>1</sub> is a number from 2 to 50;

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component e) is a product obtainable by reacting a product, obtained by reacting a polyamine of the formula VIa with cyanuric chloride, with a compound of the formula VIb



in which  $n_5'$ ,  $n_5''$  and  $n_5'''$ , independently of one another, are a number from 2 to 12,  $R_{17}$  is hydrogen,  $C_1$ - $C_{12}$  alkyl,  $C_5$ - $C_{12}$  cycloalkyl, phenyl or

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6. A composition according to claim 5, in which the organic material is a polyolefin

7. A composition according to claim 5, in which the organic material is polyethylene, polypropylene or a copolymer of polyethylene or polypropylene.

8. A process for stabilizing an organic material which is sensitive to oxidative, thermal or light-induced degradation, which comprises incorporating, a stabilizer mixture according to claim 1 into the organic material.

9. A stabilizer mixture according to claim 1, which comprises components a) and e) in a weight ratio of 5:1 to 1:5.

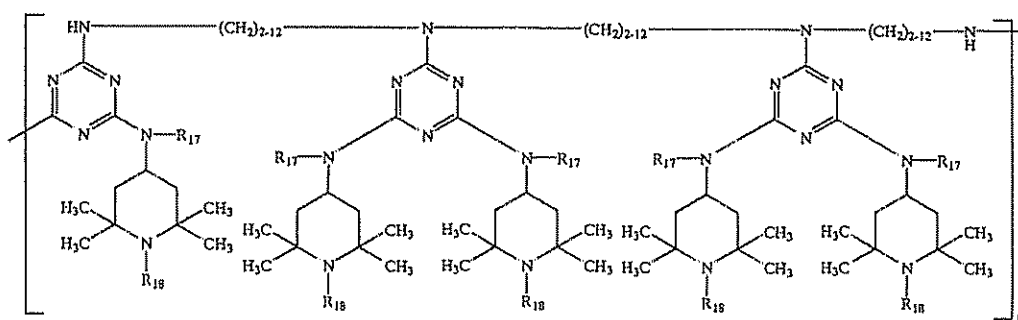
10. A stabilizer mixture according to claim 1 comprising a component a) and a component e)

where

$R_2$  is  $C_1$ - $C_{10}$  alkylene and

e) is a compound of formula VI

(VI)



$C_7$ - $C_{10}$ phenylalkyl, and  $R_{18}$  is hydrogen,  $C_1$ - $C_6$ alkyl, O,  $-\text{CH}_2\text{CN}$ ,  $C_3$ - $C_6$ alkenyl,  $C_7$ - $C_{10}$ phenylalkyl,  $C_7$ - $C_{10}$ phenylalkyl which is substituted by  $C_1$ - $C_4$ alkyl on the phenyl radical, or  $C_1$ - $C_8$ acyl;

a weight ratio between component a) and component e) being about 20:1 to about 1:20.

2. A stabilizer mixture according to claim 1, in which  $R_1$  is hydrogen,  $R_2$  is ethylene and  $n_5$  is a number from 2 to 25

3. A stabilizer mixture according to claim 1, in which  $n_5'$ ,  $n_5''$  and  $n_5'''$ , independently of one another, are a number from 2 to 4,  $R_{17}$  is  $C_1$ - $C_4$ alkyl, and  $R_{18}$  is hydrogen.

4. A stabilizer mixture according to claim 1, which comprises components a) and e) in a weight ratio of 1:1

5. A composition comprising an organic material which is sensitive to oxidative, thermal or light-induced degradation and a stabilizer mixture according to claim 1

wherein

$n_5$  is 1 to 20,

$R_{18}$  is hydrogen or  $C_1$ - $C_6$ alkyl and

$R_{17}$  is hydrogen or  $C_1$ - $C_{12}$ alkyl.

11. A composition comprising an organic material which is sensitive to oxidative, thermal or light-induced degradation and a stabilizer mixture according to claim 10.

12. A composition according to claim 11, in which the organic material is a polyolefin.

13. A composition according to claim 11, in which the organic material is polyethylene, polypropylene or a copolymer of polyethylene or polypropylene.


14. A process for stabilizing an organic material which is sensitive to oxidative, thermal or light-induced degradation, which comprises incorporating a stabilizer mixture according to claim 10 into the organic material.

\* \* \* \* \*

JS 44 (Rev 11/04)

**CIVIL COVER SHEET**

The JS-44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON THE REVERSE OF THE FORM.)

<b>I. (a) PLAINTIFFS</b> Ciba Specialty Chemicals Corporation  <b>(b)</b> County of Residence of First Listed Plaintiff <u>New Castle County, DE</u> (EXCEPT IN U.S. PLAINTIFF CASES)  <b>(c)</b> Attorney's (Firm Name, Address, and Telephone Number) Chad M. Shandler Richards, Layton & Finger One Rodney Square 920 North King Street Wilmington, DE 19801 302-651-7700		<b>DEFENDANTS</b> 3V, Inc. County of Residence of First Listed Defendant <u>New Castle County, DE</u> (IN U.S. PLAINTIFF CASES ONLY)  NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE LAND INVOLVED  Attorneys (If Known)																									
<b>II. BASIS OF JURISDICTION</b> (Place an "X" in One Box Only)		<b>III. CITIZENSHIP OF PRINCIPAL PARTIES</b> (Place an "X" in One Box for Plaintiff and One Box for Defendant)																									
<input type="checkbox"/> 1 U.S. Government Plaintiff  <input type="checkbox"/> 2 U.S. Government Defendant		<input checked="" type="checkbox"/> 3 Federal Question (U.S. Government Not a Party)  <input type="checkbox"/> 4 Diversity (Indicate Citizenship of Parties in Item III)																									
		<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <th></th> <th>PTF</th> <th>DEF</th> <th></th> <th>PTF</th> <th>DEF</th> </tr> <tr> <td>Citizen of This State</td> <td><input type="checkbox"/> 1</td> <td><input type="checkbox"/> 1</td> <td>Incorporated or Principal Place of Business In This State</td> <td><input type="checkbox"/> 4</td> <td><input type="checkbox"/> 4</td> </tr> <tr> <td>Citizen of Another State</td> <td><input type="checkbox"/> 2</td> <td><input type="checkbox"/> 2</td> <td>Incorporated and Principal Place of Business In Another State</td> <td><input type="checkbox"/> 5</td> <td><input type="checkbox"/> 5</td> </tr> <tr> <td>Citizen or Subject of a Foreign Country</td> <td><input type="checkbox"/> 3</td> <td><input type="checkbox"/> 3</td> <td>Foreign Nation</td> <td><input type="checkbox"/> 6</td> <td><input type="checkbox"/> 6</td> </tr> </table>			PTF	DEF		PTF	DEF	Citizen of This State	<input type="checkbox"/> 1	<input type="checkbox"/> 1	Incorporated or Principal Place of Business In This State	<input type="checkbox"/> 4	<input type="checkbox"/> 4	Citizen of Another State	<input type="checkbox"/> 2	<input type="checkbox"/> 2	Incorporated and Principal Place of Business In Another State	<input type="checkbox"/> 5	<input type="checkbox"/> 5	Citizen or Subject of a Foreign Country	<input type="checkbox"/> 3	<input type="checkbox"/> 3	Foreign Nation	<input type="checkbox"/> 6	<input type="checkbox"/> 6
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<b>IV. NATURE OF SUIT</b> (Place an "X" in One Box Only)																											
<b>CONTRACT</b> <input type="checkbox"/> 110 Insurance <input type="checkbox"/> 120 Marine <input type="checkbox"/> 130 Miller Act <input type="checkbox"/> 140 Negotiable Instrument <input type="checkbox"/> 150 Recovery of Overpayment & Enforcement of Judgment <input type="checkbox"/> 151 Medicare Act <input type="checkbox"/> 152 Recovery of Defaulted Student Loans (excl. Veterans) <input type="checkbox"/> 153 Recovery of Overpayment of Veteran's Benefits <input type="checkbox"/> 160 Stockholder's Suits <input type="checkbox"/> 190 Other Contract <input type="checkbox"/> 195 Contract Product Liability <input type="checkbox"/> 196 Franchise  <b>REAL PROPERTY</b> <input type="checkbox"/> 210 Land Condemnation <input type="checkbox"/> 220 Foreclosure <input type="checkbox"/> 230 Rent Lease & Eject <input type="checkbox"/> 240 Torts to Land <input type="checkbox"/> 245 Tort Product Liability <input type="checkbox"/> 290 All Other Real Property	<b>PERSONAL INJURY</b> <input type="checkbox"/> 310 Airplane <input type="checkbox"/> 315 Airplane Product Liability <input type="checkbox"/> 320 Assault, Libel & Slander <input type="checkbox"/> 330 Federal Employers' Liability <input type="checkbox"/> 340 Marine <input type="checkbox"/> 345 Marine Product Liability <input type="checkbox"/> 350 Motor Vehicle <input type="checkbox"/> 355 Motor Vehicle Product Liability <input type="checkbox"/> 360 Other Personal Injury  <b>CIVIL RIGHTS</b> <input type="checkbox"/> 441 Voting <input type="checkbox"/> 442 Employment <input type="checkbox"/> 443 Housing/Accommodations <input type="checkbox"/> 444 Welfare <input type="checkbox"/> 445 Amer. w/Disabilities - Employment <input type="checkbox"/> 446 Amer. w/Disabilities - Other <input type="checkbox"/> 440 Other Civil Rights	<b>PERSONAL INJURY</b> <input type="checkbox"/> 362 Personal Injury - Med. Malpractice <input type="checkbox"/> 365 Personal Injury - Product Liability <input type="checkbox"/> 368 Asbestos Personal Injury Product Liability  <b>PERSONAL PROPERTY</b> <input type="checkbox"/> 370 Other Fraud <input type="checkbox"/> 371 Truth In Lending <input type="checkbox"/> 380 Other Personal Property Damage <input type="checkbox"/> 385 Property Damage Product Liability  <b>PRISONER PETITIONS</b> <input type="checkbox"/> 510 Motions to Vacate Sentence Habeas Corpus: <input type="checkbox"/> 530 General <input type="checkbox"/> 535 Death Penalty <input type="checkbox"/> 540 Mandamus & Other <input type="checkbox"/> 550 Civil Rights <input type="checkbox"/> 555 Prison Condition	<b>FORFEITURE/PENALTY</b> <input type="checkbox"/> 610 Agriculture <input type="checkbox"/> 620 Other Food & Drug <input type="checkbox"/> 625 Drug Related Seizure of Property 21 USC 881 <input type="checkbox"/> 630 Liquor Laws <input type="checkbox"/> 640 R.R. & Truck <input type="checkbox"/> 650 Airline Regs. <input type="checkbox"/> 660 Occupational Safety/Health <input type="checkbox"/> 690 Other  <b>LABOR</b> <input type="checkbox"/> 710 Fair Labor Standards Act <input type="checkbox"/> 720 Labor/Mgmt. Relations <input type="checkbox"/> 730 Labor/Mgmt. Reporting & Disclosure Act <input type="checkbox"/> 740 Railway Labor Act <input type="checkbox"/> 790 Other Labor Litigation <input type="checkbox"/> 791 Empl. Ret. Inc. Security Act																								
<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <th style="width: 25%;">BANKRUPTCY</th> <th style="width: 25%;">OTHER STATUTES</th> </tr> <tr> <td> <input type="checkbox"/> 422 Appeal                      28 USC 158  <input type="checkbox"/> 423 Withdrawal                      28 USC 157   <b>PROPERTY RIGHTS</b>  <input type="checkbox"/> 820 Copyrights  <input checked="" type="checkbox"/> 830 Patent  <input type="checkbox"/> 840 Trademark   <b>SOCIAL SECURITY</b>  <input type="checkbox"/> 861 HIA (1395ff)  <input type="checkbox"/> 862 Black Lung (923)  <input type="checkbox"/> 863 DIWC/DIWW (405(g))  <input type="checkbox"/> 864 SSID Title XVI  <input type="checkbox"/> 865 RSI (405(g))   <b>FEDERAL TAX SUITS</b>  <input type="checkbox"/> 870 Taxes (U.S. Plaintiff or Defendant)  <input type="checkbox"/> 871 IRS - Third Party 26 USC 7609             </td> <td> <input type="checkbox"/> 400 State Reappointment  <input type="checkbox"/> 410 Antitrust  <input type="checkbox"/> 430 Banks and Banking  <input type="checkbox"/> 450 Commerce  <input type="checkbox"/> 460 Deportation  <input type="checkbox"/> 470 Racketeer Influenced and Corrupt Organizations  <input type="checkbox"/> 480 Consumer Credit  <input type="checkbox"/> 490 Cable/Sat TV  <input type="checkbox"/> 810 Selective Service  <input type="checkbox"/> 850 Securities/Commodities/Exchange  <input type="checkbox"/> 875 Customer Challenge                      12 USC 3410  <input type="checkbox"/> 890 Other Statutory Actions  <input type="checkbox"/> 891 Agricultural Acts  <input type="checkbox"/> 892 Economic Stabilization Act  <input type="checkbox"/> 893 Environmental Matters  <input type="checkbox"/> 894 Energy Allocation Act  <input type="checkbox"/> 895 Freedom of Information Act  <input type="checkbox"/> 900 Appeal of Fee Determination Under Equal Access to Justice  <input type="checkbox"/> 950 Constitutionality of State Statutes             </td> </tr> </table>				BANKRUPTCY	OTHER STATUTES	<input type="checkbox"/> 422 Appeal 28 USC 158 <input type="checkbox"/> 423 Withdrawal 28 USC 157  <b>PROPERTY RIGHTS</b> <input type="checkbox"/> 820 Copyrights <input checked="" type="checkbox"/> 830 Patent <input type="checkbox"/> 840 Trademark  <b>SOCIAL SECURITY</b> <input type="checkbox"/> 861 HIA (1395ff) <input type="checkbox"/> 862 Black Lung (923) <input type="checkbox"/> 863 DIWC/DIWW (405(g)) <input type="checkbox"/> 864 SSID Title XVI <input type="checkbox"/> 865 RSI (405(g))  <b>FEDERAL TAX SUITS</b> <input type="checkbox"/> 870 Taxes (U.S. Plaintiff or Defendant) <input type="checkbox"/> 871 IRS - Third Party 26 USC 7609	<input type="checkbox"/> 400 State Reappointment <input type="checkbox"/> 410 Antitrust <input type="checkbox"/> 430 Banks and Banking <input type="checkbox"/> 450 Commerce <input type="checkbox"/> 460 Deportation <input type="checkbox"/> 470 Racketeer Influenced and Corrupt Organizations <input type="checkbox"/> 480 Consumer Credit <input type="checkbox"/> 490 Cable/Sat TV <input type="checkbox"/> 810 Selective Service <input type="checkbox"/> 850 Securities/Commodities/Exchange <input type="checkbox"/> 875 Customer Challenge 12 USC 3410 <input type="checkbox"/> 890 Other Statutory Actions <input type="checkbox"/> 891 Agricultural Acts <input type="checkbox"/> 892 Economic Stabilization Act <input type="checkbox"/> 893 Environmental Matters <input type="checkbox"/> 894 Energy Allocation Act <input type="checkbox"/> 895 Freedom of Information Act <input type="checkbox"/> 900 Appeal of Fee Determination Under Equal Access to Justice <input type="checkbox"/> 950 Constitutionality of State Statutes																				
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<b>V. ORIGIN</b> (Place an "X" in One Box Only)																											
<input checked="" type="checkbox"/> Original Proceeding <input type="checkbox"/> 2 Removed from State Court <input type="checkbox"/> 3 Remanded from Appellate Court <input type="checkbox"/> 4 Reinstated or Reopened <input type="checkbox"/> 5 Transferred from another district (specify) <input type="checkbox"/> 6 Multidistrict Litigation <input type="checkbox"/> 7 Appeal to District Judge from Magistrate Justice																											
<b>VI. CAUSE OF ACTION</b>		Cite the U.S. Civil Statute under which you are filing (Do not cite jurisdictional statutes unless diversity): <u>35 U.S.C. §291</u> Brief description of cause: <u>Action under patent laws for declaratory relief</u>																									
<b>VII. REQUESTED IN COMPLAINT</b>		CHECK IF THIS IS A CLASS ACTION UNDER F.R.C.P. 23 <input type="checkbox"/> DEMAND \$ _____ CHECK YES only if demanded in complaint: JURY DEMAND: <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No																									
<b>VIII. RELATED CASE(S) IF ANY</b> (See instructions): JUDGE <u>Joseph J. Farnan, Jr.</u> DOCKET NUMBER <u>06-00593-JJF; 06-00629-JJF</u>		DATE <u>October 31, 2006</u> SIGNATURE OF ATTORNEY OF RECORD 																									
<b>FOR OFFICE USE ONLY</b> RECEIPT # _____ AMOUNT _____ APPL. YING IFP _____ JUDGE _____ MAG. JUDGE _____																											

AO FORM 85 RECEIPT (REV. 9/04)

United States District Court for the District of Delaware

Civil Action No. 06 - 672

**ACKNOWLEDGMENT**  
**OF RECEIPT FOR AO FORM 85**

**NOTICE OF AVAILABILITY OF A**  
**UNITED STATES MAGISTRATE JUDGE**  
**TO EXERCISE JURISDICTION**

I HEREBY ACKNOWLEDGE RECEIPT OF 1 COPIES OF AO FORM 85.

10/31/06

(Date forms issued)

Greg Pierce

(Signature of Party or their Representative)

Greg Pierce

(Printed name of Party or their Representative)

**Note: Completed receipt will be filed in the Civil Action**